



Study of collective excitations and Schottky barrier formations at III-V semiconductor surfaces and interfaces

by Yuan Meng

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

Montana State University

© Copyright by Yuan Meng (1991)

Abstract:

High resolution electron energy loss spectroscopy and synchrotron radiation photoemission have been used to study collective excitations and Schottky barrier formation at III-V semiconductor surfaces and interfaces.

First, we studied the hole plasmon excitations in the valence-band of heavily doped p-GaAs(110) surfaces ($2.2 \times 10^{19} / \text{cm}^3$), using HREELS. For the first time, a single well defined surface hole plasmon peak is observed. The quantitative analysis in a framework of the classical dielectric theory reveals this peak is attributed to a coherent excitation of both light-hole and heavy-hole plasmas. A dramatic temperature effect for the surface hole plasmon peak is also observed. We show that this temperature effect is due to the surface scattering process, in conjunction with the kinematical factor.

We also studied the collective excitations in the overlayer systems, such as Bi/GaAs(110), ZnSe/GaAs(110), using HREELS. The overlayer excitation modes, such as the Bi two-dimensional electron plasmon mode, and the overlayer ZnSe mode were observed. Within a framework of the classical dielectric theory, a multi-layer model is employed. Good agreement is obtained between experiments and the theory. The data analysis shows that the Bi overlayer undergoes a transition from a semiconductor to a semimetal at the coverage of 1.5 ML; the ZnSe long wavelength optical phonon excitation exists in an ultrathin overlayer (1-2 ML). In addition, both experimental results and associated calculations of the ZnSe/Bi/GaAs(110) sandwich system are also presented.

Finally, we studied the Schottky barrier formation at both Bi/n- and p-InP(110) interfaces, using synchrotron radiation photoemission spectroscopy. A unique band bending is observed in the region of few monolayers for the two cases. It is found that, at 1 ML of Bi, the band bending almost vanishes for Bi/n-InP, while it remains significantly large for p-InP. We show that the large band bending for p-InP at 1 ML is due to the charge transfer process from the Bi induced states to the InP substrate. A quantitative analysis of high-resolution core levels is also carried out in determining the interface structure.

STUDY OF COLLECTIVE EXCITATIONS AND SCHOTTKY BARRIER
FORMATIONS AT III-V SEMICONDUCTOR SURFACES AND INTERFACES

by

Yuan Meng

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Doctor of Philosophy

in

Physics

MONTANA STATE UNIVERSITY
Bozeman, Montana

June, 1991

D378
m525

APPROVAL

of a thesis submitted by

Yuan Meng

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Date

6/9 5/91

Chairperson, Graduate committee

Lerald Lopez

Approved for the Major Department

Date

6-15-91

Head, Major Department

Wernimann

Approved for the College of Graduate Studies

Date

July 25, 1991

Graduate Dean

Henry L. Parsons

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a doctoral degree at Montana State University, I agree that the library shall make it available to borrowers under rules of the Library. I further agree that copying of this thesis is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U. S. Copyright Law. Requests for extensive copying or reproduction of the thesis should be referred to University Microfilms International, 300 North Zeeb Road, Ann Arbor, Michigan 48106, to whom I have granted "the exclusive right to reproduce and distribute copies of the dissertation in and from microfilm and the right to reproduce and distribute by abstract in any format."

Signature



Date

6-15-91

DEDICATED TO MY PARENTS

VITA

Yuan Meng, was born in Shanghai, China on December 30, 1960, the son of Shishun Meng and Yuanxiang Liu. He has two brothers, Ning and Mu.

Yuan had a happy childhood at Shanghai, where he stayed with his grandparents. After he graduated from Baogang 1st High School at Baotou, Inner Mongolia in 1976, he worked for a metallurgical construction company at Tangshan, Hebei. Two years later, he was admitted by Huazhong University of Science and Technology, Wuhan, Hubei, where he received the Bachelor and Master of Engineering degree in semiconductor devices and materials.

After two years being a research associate in the Department of Solid-State Electronics, Huazhong University of Science and Technology, in 1986 he entered the graduate school at Montana State University, Bozeman, Montana, where he has been until the present.

ACKNOWLEDGEMENTS

I am grateful for the guidance and support of my thesis adviser, Dr. Gerald J. Lapeyre. Many times when I got stuck in solving problems and went to him for advice, the discussion with him always turned out to give an answer, or at least open a new gate for thinking. His sense of how to deal with a physics problem, was great help in my thesis work. I wish to thank Dr. James R. Anderson for many things from experimental advice to the initiation of the hole plasmon project. His experimental knowledge in surface science was a valuable asset to my training. His critical reading of my manuscripts and this thesis is especially appreciated. I also acknowledge Dr. John Hermanson for the guidance in the theoretical aspect of the HREELS work in this thesis. His comments on my manuscripts and this thesis are greatly appreciated.

I would like to thank Drs. J. Joyce, M. Nelson, and M. Tang, with whom I learned a great deal of the synchrotron radiation photoemission technique. I would also like to thank Drs. Y. Chen, A. Eguluz, J. Schaefer, and J. Gaspar for stimulating discussions of HREELS matters.

I would also like to thank Mr. John Lapeyre for his reading and correcting this thesis. Valuable technical support provided by Milt Jaehnig, Andrew Paule is appreciated. My special thanks go to Ms. Linda Todd and Robyn Klein for their kind help and kindness.

TABLE OF CONTENTS

APPROVAL	ii
STATEMENT OF PERMISSION TO USE	iii
VITA	v
ACKNOWLEDGEMENTS	vi
TABLE OF CONTENTS	vii
LIST OF TABLES	x
LIST OF FIGURES	xi
ABSTRACT	xiv
 I. INTRODUCTION	 1
Surface Hole Plasma	2
Collective Excitations in Overlayer Systems	4
Schottky Barrier Formation	7
 II. EXPERIMENTAL TECHNIQUES AND PROCEDURES	 12
High Resolution Electron Energy Loss Spectroscopy	12
HREELS setup	12
HREELS spectrometer	14
Comments on techniques	17
Synchrotron Radiation Photoemission Spectroscopy	18
Synchrotron radiation source	18
Photon energy monochromator	19
Electron energy analyzer	21
Sample Preparations	21
Doping density selection	21
Clean surface preparations	23

TABLE OF CONTENTS-CONTINUED

Overlayer and H-adsorbed sample preparations	23
III. PHOTOEMISSION MEASUREMENT AND DATA ANALYSIS	25
Principle of Measurement	25
Core-level measurement for interface studies	25
Measurement of Fermi-level study	27
Quantitative Analysis Procedures	30
Core-level data analysis	31
Fermi-level determination	33
IV. BASIC THEORY OF HREELS	35
Theoretical Aspects	35
Further Discussion	42
Penetration depth	43
Kinematical factor	44
V. HOLE PLASMON EXCITATIONS	46
Introduction	46
Surface Hole Plasma	49
Observation	49
Equivalent hole plasmon	52
Discussion of the peak width	53
Effect of kinematical factor	56
Temperature Effect	57
Observation	57
Commentary	59
Data analysis	60
Scattering rate	60
Other effects for kinematical factor	63
Interface Hole Plasmon	65
Interface plasmon mode	65
Observation of "dead layer" in p-GaAs	68
VI. COLLECTIVE EXCITATIONS IN OVERLAYER SYSTEMS	73
Interface Structure	73

TABLE OF CONTENTS-CONTINUED

Bi/GaAs(110) System	75
Experimental results	76
Discussions and modelling	79
ZnSe/GaAs(110) Interfaces	87
Experimental results	87
Discussions and modelling	90
ZnSe/Bi/GaAs(110) Systems	98
Results and discussions	99
 VII. SCHOTTKY BARRIER FORMATION STUDY	 104
Introduction	104
Interface Structures	109
Coverage Dependence of Band Bending	111
Band bending studies	111
Electronic structure studies	116
Charge Transfer Model	119
Low coverage case	119
High coverage case	122
Schottky Barrier Model for Bi/InP(110)	124
 VIII. CONCLUSION	 126
REFERENCES	130

LIST OF TABLES

Table		Page
I	The values relevant to the surface hole plasmon for $p=1\times 10^{19} / \text{cm}^3$ and $p=2.2\times 10^{19} / \text{cm}^3$	51
II	Parameters of Bi overlayer obtained from fitting of experimental data . .	83

LIST OF FIGURES

Figure		Page
1.	Schematic model for an overlayer-substrate system	5
2.	Schematics of the HREELS experimental chamber	13
3.	Schematics of 127° cylindrical double pass HREELS spectrometer	15
4.	Optical layout of Ames/Montana ERG/Seya monochromator	20
5.	Schematics of the angle-resolving double pass CMA	22
6.	HREELS principle and definition of the geometrical parameters	37
7.	A HREELS spectrum of a fresh-cleaved p-GaAs(110) surface at 80 K . .	50
8.	The calculated HREELS spectra (solid curves) for three approximations of the dielectric function	55
9.	Temperature dependent HREELS spectra for a clean heavily doped p-GaAs(110) surface taken in a cyclic manner	58
10.	The calculated HREELS spectra of p-GaAs(110) with Γ (A) 64 meV, (B) 74 meV, and (C) 86 meV	61
11.	The bulk and surface scattering rates of holes with temperature	62
12.	The HREELS spectra of p-GaAs(110) before and after hydrogen exposure	67
13.	HREELS spectra of p-GaAs(110) with different primary energies taken at room temperature	70
14.	The calculated HREELS spectrum for the case of Ref. 7 using a two-layer model	71
15.	HREELS spectra of the Bi/n-GaAs(110) interface for the clean GaAs(110) surface and several Bi coverages from 0 to 10 ML	77
16.	Two HREELS spectra of Bi/n-GaAs(110) with coverages of 0.1 ML and 4 ML in a smaller energy scale	78

LIST OF FIGURES-CONTINUED

Figure		Page
17	The schematic for the Bi/n-GaAs(110) interface morphology and the model for HREELS calculations	80
18	The calculated HREELS spectra of n-GaAs(110) as a function of Bi coverages with a three-layer model	82
19.	HREELS spectra of a clean n-GaAs(110) surface and after deposition of ZnSe of 3 and 18 ML	88
20.	HREELS spectra of the phonon losses at ~30 meV taken for various ZnSe coverages	91
21.	The calculated HREELS spectra for several ZnSe coverages using a three-layer model	93
22.	The calculated HREELS spectra for several ZnSe coverages after taking into account of an instrument broadening of 6 meV	95
23.	Composite peak position vs ZnSe coverage	96
24	HREELS spectra of the ZnSe/Bi/n-GaAs(110) sandwich system for several ZnSe coverages from 0 to 11 ML	100
25.	The calculated HREELS spectra for several ZnSe coverages on Bi/GaAs(110) using a four-layer model	101
26.	Schematic of band bending before and after metal-semiconductor contact	105
27.	In 4d and P 2p core level EDC's with Bi deposition at 300 K	110
28.	Bi 5d core level EDC's with Bi deposition at 300 K	112
29.	Position of surface Fermi level vs. Bi coverage on both n- and p-InP(110)	114
30.	Angle-integrated EDCs for the Bi/n-InP(110) taken at room temperature for various Bi coverages	117

LIST OF FIGURES-CONTINUED

Figure	Page
31. EDC's of the emission edge for Bi on n- and p-InP(110)	118
32. Energy-level diagrams of InP and schematic densities of states of the Bi overlayer on n- and p-InP(110) at 1 ML	121
33. High coverage EDC's of the emission edge for Bi/n-InP	123

ABSTRACT

High resolution electron energy loss spectroscopy and synchrotron radiation photoemission have been used to study collective excitations and Schottky barrier formation at III-V semiconductor surfaces and interfaces.

First, we studied the hole plasmon excitations in the valence-band of heavily doped p-GaAs(110) surfaces ($2.2 \times 10^{19} / \text{cm}^3$), using HREELS. For the first time, a single well defined surface hole plasmon peak is observed. The quantitative analysis in a framework of the classical dielectric theory reveals this peak is attributed to a coherent excitation of both light-hole and heavy-hole plasmas. A dramatic temperature effect for the surface hole plasmon peak is also observed. We show that this temperature effect is due to the surface scattering process, in conjunction with the kinematical factor.

We also studied the collective excitations in the overlayer systems, such as Bi/GaAs(110), ZnSe/GaAs(110), using HREELS. The overlayer excitation modes, such as the Bi two-dimensional electron plasmon mode, and the overlayer ZnSe mode were observed. Within a framework of the classical dielectric theory, a multi-layer model is employed. Good agreement is obtained between experiments and the theory. The data analysis shows that the Bi overlayer undergoes a transition from a semiconductor to a semimetal at the coverage of 1.5 ML; the ZnSe long wavelength optical phonon excitation exists in an ultrathin overlayer (1-2 ML). In addition, both experimental results and associated calculations of the ZnSe/Bi/GaAs(110) sandwich system are also presented.

Finally, we studied the Schottky barrier formation at both Bi/n- and p-InP(110) interfaces, using synchrotron radiation photoemission spectroscopy. A unique band bending is observed in the region of few monolayers for the two cases. It is found that, at 1 ML of Bi, the band bending almost vanishes for Bi/n-InP, while it remains significantly large for p-InP. We show that the large band bending for p-InP at 1 ML is due to the charge transfer process from the Bi induced states to the InP substrate. A quantitative analysis of high-resolution core levels is also carried out in determining the interface structure.

CHAPTER I

INTRODUCTION

The microscopic properties of semiconductor surfaces and interfaces are a fundamental field of investigation in solid state physics, with great practical importance in semiconductor technology. Understanding of these interesting physical properties may eventually lead not only to novel approaches as to technologically important issues, but also to the extension of our fundamental knowledge (e.g., the quantum Hall effect). The principal focus of this thesis is to study the properties of III-V semiconductor surfaces and interfaces which have been the subjects of intense studies for 30 years, by an extensive use of state-of-the-art surface-sensitive experimental probes, such as high-resolution electron energy loss spectroscopy (HREELS), and synchrotron radiation photoemission spectroscopy. The emphasis of the work presented in the thesis is in the following areas: surface hole plasma, collective excitations in overlayer systems, Schottky barrier formation.

Surface Hole Plasma

Considerable attention has been given recently to the study of the surface plasmon excitations of free carriers in doped semiconductors using high-resolution electron energy-loss spectroscopy (HREELS). A number of experimental and theoretical investigations have been carried out on this subject, since Matz and Lüth first observed the surface plasmon in the conduction band of an n-type GaAs(110) surface.¹⁻²⁴ Most of these studies focused on the electron plasmon in the conduction band. However, from a physical standpoint, the hole plasma in the valence band is also of interest, because its understanding may eventually lead to both fundamental knowledge of the nature of the hole, and an understanding of the dynamical response of a system in which two types of free carriers (light and heavy holes) are present. Egdell, *et al*⁷ reported pioneering HREELS studies searching for the surface hole plasma in the valence band on MBE-grown p-GaAs(100). Because of the difference of effective masses of electrons and holes, they chose a high doping density $\sim 1.0 \times 10^{19} \text{ cm}^{-3}$ which was expected to be large enough for the loss peaks due to the surface hole plasma to emerge from the elastic peak background, in accordance with their experience in observing the electron plasma. However, contrary to their expectation, the loss spectrum showed no well-defined hole-plasmon loss peaks. It has remained unclear whether this result is due to technical problems or the intrinsic complexity of the hole plasmon excitations. In fact, so far, not only for the GaAs system, but for all

other semiconductors, no direct observation of the hole plasmon has been reported.

In this thesis we present the first observation of the surface hole plasmon in the valence band of a p-GaAs(110) surface.⁸ We find that the contribution of the surface light-hole and heavy-hole plasmas to the inelastic scattering process can be considered as a coherent excitation of both the light-hole and heavy-hole plasmas; only one single peak due to the hole plasmas is observed in the loss spectra. Compared to a typical conduction-band electron plasmon,¹² the hole-plasmon oscillation has a significantly large damping term (or scattering rate), so that in some cases the hole plasmon oscillation can even be damped out, which implies that the well defined hole-plasmon loss feature might not be observed.

It is particularly interesting to study the temperature-dependent effects of semiconductor surfaces, since many electronic properties of semiconductors are strongly dependent on temperature. Previous studies on conduction-band surface plasmas on Si(111)7×7^{13,25} have shown that the electronic structure of the surface depends strongly on temperature; the temperature dependence of the width of the quasielastic peak can be used to obtain information regarding the surface free-carrier density, surface effective mass, and the surface conductivity.

In this thesis we study the temperature dependence of the surface hole plasmas in p-type GaAs(110). A reversible temperature effect for the surface hole plasmon peak is observed.²⁶ This temperature effect is found to be due to the temperature dependence of the surface scattering process, in conjunction with the kinematical

factor, and not the thermal activation.

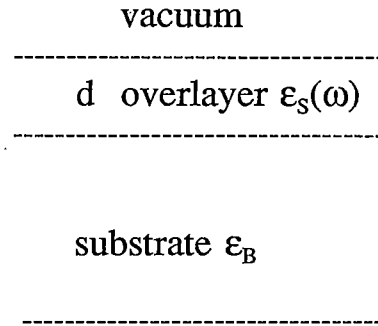
Collective Excitations in Overlayer Systems

It has recently been shown that high-resolution electron energy-loss spectroscopy (HREELS) is useful for studying semiconducting or (semi)metallic overlayers on semiconductors.^{27-30,32,43,87,88} For instance, from the observation of collective interface modes, such as the plasmon mode in the overlayer, information about transport parameters can be extracted.²⁷⁻³⁰ It is therefore of general interest to understand the collective excitations (e.g., phonons and plasmas in semiconducting or (semi)metallic overlayers on semiconductor surfaces), their dispersion, their interaction with other modes and how they are influenced by film roughness, mode of growth, etc.

From a physical standpoint, the overlayer collective excitations are of particular interest, because they have some novel properties which bulk and surface excitations do not have. Figure 1 shows an overlayer with a thickness d characterized by a dielectric constant $\epsilon_s(\omega)$, below which is the semi-infinite substrate with a complex (but isotropic) dielectric constant ϵ_B (ϵ_B here is assumed to be frequency independent in order to exhibit the intrinsic properties of the overlayer). Let us first consider the case where the overlayer thickness is large (i.e., $Q_1 d \gg 1$), so that the overlayer system simulates a nearly semi-infinite material adjacent to both the vacuum

and medium ϵ_B ; the excitation modes approach the modes that are localized at the boundary between two semi-infinite materials whose frequencies are given by the condition

$$\epsilon_s(\omega) = -\epsilon_{\text{outside}} \quad (1.1)$$



where $\epsilon_{\text{outside}}$ is the appropriate dielectric

constant of the adjacent medium, i.e., 1 or ϵ_B in the present case.⁴ However,

with decreasing the overlayer thickness, these two localized modes start to "see" each other so that a coupling between these two modes occurs. As a result, for the case $Q_{\parallel}d \ll 1$, these two modes are completely delocalized, and transformed into two new modes. For instance, for a plasmon excitation in the overlayer, in the limit of $Q_{\parallel}d \gg 1$, the two modes near the boundaries have frequencies $\omega_p/\sqrt{2}$, and $\omega_p/\sqrt{(1+\epsilon_B)}$, respectively; while in the limit of $Q_{\parallel}d \ll 1$, because of the strong coupling between these two modes, one lies very close to ω_p (the bulk plasmon frequency, where $\epsilon_s(\omega)=0$) with a weak dependence on $Q_{\parallel}d$; the other one, however, is described by a two-dimensional dispersion relation $\omega = \omega_p \sqrt{(Q_{\parallel}d/(1+\epsilon_B))}$ which vanishes as $Q_{\parallel}$ or $d \rightarrow 0$.³⁰ Thus, one can see that these two modes, unlike the surface-like modes, now depend not only on the bulk plasmon frequency, but also on the

Fig. 1 Schematic model for an overlayer-substrate system

product of $Q_{\parallel}$ and d , which is characteristic of an overlayer.

It is also interesting to examine the collective excitations in an overlayer system as a means for exploring the initial development of the morphology, electronic structure and vibration properties of the overlayer. For instance, one can examine the overlayer plasmon excitations to study the overlayer electronic structure, and transport properties; and one can examine the phonon excitations to study the morphology and vibration properties of the overlayer.^{27,88}

However, the studies of the collective excitations in a system of overlayers on semiconductor substrates are not as well developed as for clean surfaces, especially from the experimental point of view. The main reason for this is the difficulties in experimentally preparing an interface to which a suitable theory can be applied, i.e. a nearly ideal atomically smooth overlayer. These difficulties arise because most of the III-V semiconductor related interfaces are reactive or disruptive.⁷³

→ The Bi/GaAs(110) and ZnSe/GaAs(110) interfaces are among the few materials that are found to form ordered and nondisruptive overlayers on III-V-compound semiconductor substrates, and thus they provide a good opportunity to study the collective excitations of the overlayers.³³⁻⁴³

In studying these two systems in this thesis, we use HREELS as a probe to study the physical properties of the overlayer collective excitations, e.g., plasmon and phonon excitations. We also examine these excitations to characterize these ultrathin films. We present our observations of the two-dimensional plasmon in the

Bi/GaAs(110) system,³¹ and the experimental observations of surface and interface optical phonons in the ZnSe/GaAs(110) system.⁴³ Good agreement is obtained between the experimental results and the classical dielectric theory for these two systems, which suggests that these two systems are well characteristic. By examining the overlayer electron plasmon mode as a function of Bi coverage, we find that the electronic structure of the Bi overlayer on GaAs(110) has a strong size effect due to Bi two-dimensional patches. In addition, we study a very interesting system: the ZnSe/Bi/GaAs multi-layer system, which is found to be very useful in studying the initial development of the ZnSe long-wave-length optical phonon on a scale of one monolayer.

Schottky Barrier Formation

The phenomenon of Schottky barrier formation at metal-semiconductor interfaces has remained a subject of high scientific and technological interest in condensed matter physics for over five decades.⁴⁴⁻⁷³ In 1938 Schottky first presented perhaps the simplest model for this phenomenon, i.e., the potential difference between Fermi levels in the semiconductor and metal falls entirely across the space-charge region within the semiconductor surface.⁴⁴ However, barrier-height measurements for different metals on a given semiconductor provided little evidence for such systematic behavior. The failure of the Schottky model to describe observed barrier height was

addressed by Bardeen in 1947,⁴⁵ who pointed out that there are some types of localized states at the semiconductor surface which could accumulate charge at the interface and could thereby accommodate the contact potential difference between metal and semiconductor (i.e., through a process called Fermi-level pinning). Since then, numerous studies have attempted to elucidate the origin of those localized surface states. For a long time, the Fermi-level pinning and associated band bending within the surface space charge region of the semiconductor had been regarded as consequences of intrinsic surface states at semiconductor surfaces, such as Tamm states.⁴⁶ However, experimental studies of semiconductor surfaces carried out under ultrahigh vacuum condition have revealed that some semiconductor surfaces, such as the clean cleaved (110) surfaces of most III-V semiconductors, could be free of surface states in the band-gap. Thus, many studies have focused on the process in which the metal and semiconductor are brought into contact.

Heine, in 1965, pointed out that these localized surface states at metal-semiconductor interfaces may be the metal-induced gap states (MIGS) that develop when a metal is deposited on the semiconductor surface.^{47,48} These MIGS are associated with the tails of the conduction-electron wave functions in the metal which tunnel into the band gap of the semiconductor at the interface. Heine also discussed the effect of these tails on the Schottky barrier height. The calculations based on this model developed in the 70's appeared to be quite consistent with the experimental evidence that the Schottky barrier height is much less dependent on the metal work

function for covalent materials such as Si and GaAs than for the ionic ones like ZnSe and ZnS. However, the barrier heights established for most metals on clean GaAs and InP are inconsistent with the MIGS model.

Spicer *et al.*, in 1980, proposed that Schottky barrier heights at metal-semiconductor interfaces are nearly always determined by defects at the interface. In this so-called 'unified defect model' it is assumed that the defects are generated near the semiconductor surface when the metal is deposited on the surface.^{49,50} These defects in turn lead to pinning of the Fermi level. Calculations of the energy levels associated with anion vacancies and anti-site defects such as cations on anion sites lead to a reasonable description of the Schottky barrier heights for Au on many III-V semiconductor surfaces. However, this model still cannot serve the purpose of interpreting a large amount of experimental data.

Recent studies using surface-sensitive UHV techniques indicate that the Schottky barrier heights are determined not only by the intrinsic properties of the metal and semiconductor, but also by the extrinsic features produced by the interaction between metal and semiconductor, such as chemical reaction and diffusion, defect formation, and even crystal quality.⁵²

Therefore, to exhibit the intrinsic electronic properties of a metal-semiconductor contact, one must minimize these major extrinsic contributions to the interface electronic structures. This approach is possible only if one can prepare a nearly ideal, atomically perfect interface, or at least a model interface (i.e.,

nonreactive and nondisruptive interface).⁷⁴⁻⁷⁷ The Bi/InP(110) interface, a recently discovered model interface, thus appears to be an ideal candidate for this purpose.

In this thesis, we study Schottky barrier formation at the Bi/InP(110) interface by means of high-resolution synchrotron radiation photoemission. We present a unique band bending result for Bi deposition on both n- and p-type InP(110) surfaces.⁵³ This result can be interpreted by using a charge transfer model that we proposed recently on the basis of the observed difference in the photoemission spectra of the Bi emission edges for n- and p-type samples. Our study suggests that the Bi/InP(110) system is an ideal defect free interface, and that the Schottky barrier height could be described by the Schottky model.

The thesis is organized as follows. In Chapter II, we describe experimental techniques and procedures, with emphasis on HREELS. In Chapter III, we focus on the high resolution photoemission studies, and discuss the measurement principle and data analysis procedures. In Chapter IV, we outline the basic HREELS theory, with emphasis on a discussion of several key issues in the HREELS study. In Chapter V, we study the valence-band hole plasmon excitations in p-GaAs(110) and their contribution to the dielectric response, including the observation of the surface and interface hole-plasma excitation, and an interesting temperature effect. In Chapter VI, we study the collective excitations at heterostructure interfaces, such as Bi/GaAs(110), ZnSe/GaAs(110), and ZnSe/Bi/GaAs(110) systems. In Chapter VII, we turn to a new subject, Schottky barrier formation at metal/semiconductor interfaces. We present a

unique band-bending result for the Bi/InP(110) interface, and propose a charge-transfer model to explain this result. Chapter VIII summarizes the thesis.

CHAPTER II

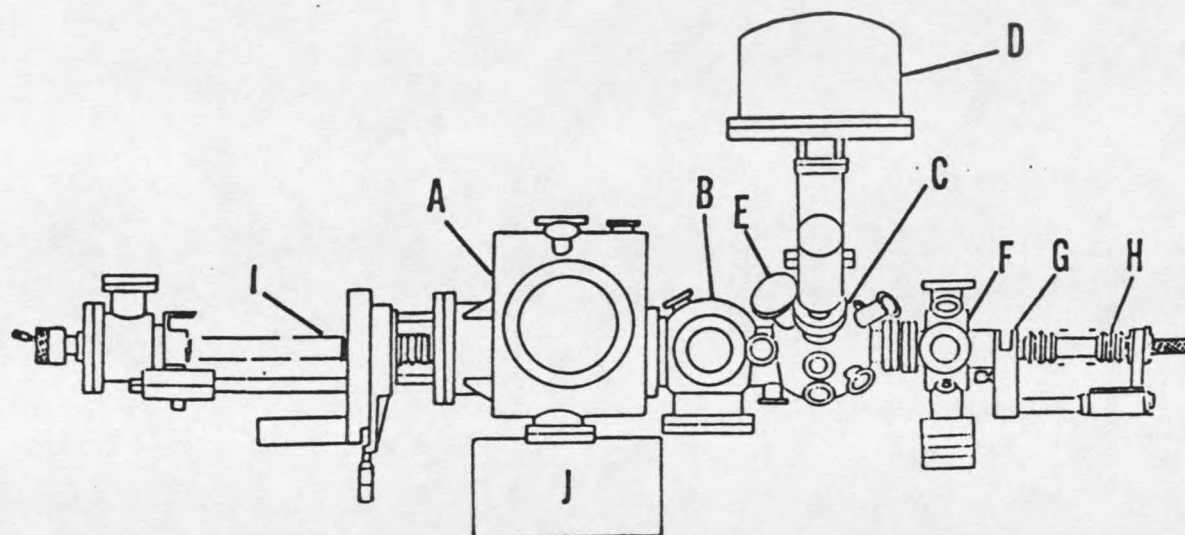
EXPERIMENTAL TECHNIQUES AND PROCEDURES

In this thesis two major surface sensitive techniques are used. One is high-resolution electron-energy-loss spectroscopy (HREELS), which was performed at the Center for Research in Surface Science (CRISS), Montana State University. The other technique is synchrotron-radiation photoemission spectroscopy, which was performed at Aladdin storage ring, University of Wisconsin-Madison. In this chapter we give a general description of these two techniques, then discuss the sample preparation procedures.

High Resolution Electron Energy Loss Spectroscopy

HREELS Setup

The HREELS experimental chamber, shown in Fig. 2 consists of a main chamber and a preparation chamber. The chamber is equipped with a high resolution electron energy loss spectrometer, a low-energy electron diffraction (LEED) system, a Leybold-Heraeus hemisphere energy analyzer, an X-ray source, an ultra-violet light



L-H LOW-ENERGY, ELECTRON-ENERGY-LOSS AND PHOTOELECTRON SPECTROMETERS

- | | |
|--|--|
| A. LEELS Analysis Chamber | E. SIMS Detector |
| B. LEED Analysis Chamber | F. Sample Preparation Chamber |
| C. ESCA, UPS, AES, SIMS Analysis Chamber | G. Fast-Entry Sample Interlock |
| D. ESCA, UPS, AES, ISS Hemispherical Energy Analyzer | H. Hot/Cold Sample Rod |
| | I. x,y,z,θ Hot/Cold Sample Manipulator |
| | J. Main Chamber Ion and Turbomolecular Pump System |

(Ion Sputter Gun and UV Lamp Omitted from Figure)

Fig. 2 Schematics of the HREELS experimental chamber

source, and an ion sputtering gun. The pumping system on the main chamber includes a Leybold 360 turbo pump backed with a Leybold mechanical pump, an ion pump, and a Ti sublimation pump with a liquid nitrogen cooled trap. The preparation chamber, which is used for fast insertion of the samples for XPS, has a turbo pump and is mechanically connected to the main chamber by a loadlock rod with a set of viton-O rings for vacuum isolation. The experimental base pressure is 10^{-10} Torr. By virtue of cryopumping, this pressure can be reduced to $3\text{--}5 \times 10^{-11}$ Torr in low temperature experiments.

HREELS spectrometer

High-resolution electron energy loss spectroscopy (HREELS) initially emerged as a new surface sensitive technique to study vibrations of surface and adsorbed molecules. The vibrational energies of the molecules span the range of some 10 meV up to some 500 meV, the linewidths being of the order of 1-10 meV. In an electron energy-loss spectroscopy experiment, in order to resolve these vibration features on such a small energy scale, both the resolution of the analyzing spectrometer, and the energy width of the primary electron beam have to meet stringent requirements. However, since no physical source of electron emission is known with an energy distribution as narrow as a few millielectron volts, an electron optical device which as an energy filter with a small energy window, i.e., a monochromator, has to be used.

A schematic of the double-pass ELS spectrometer is shown in Fig. 3, which

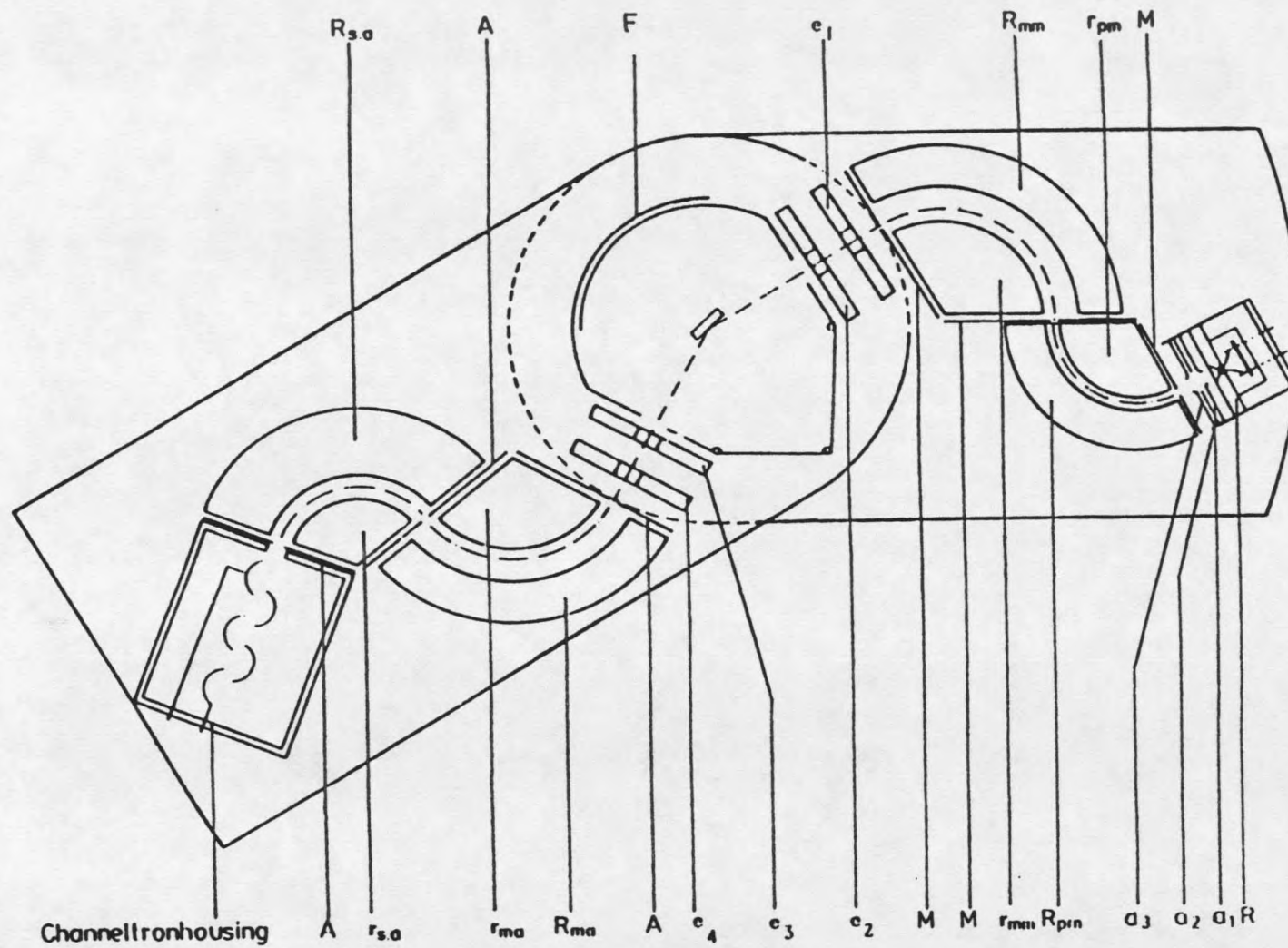


Fig. 3 Schematics of 127° cylindrical double pass HREELS spectrometer.

consists of five basic subunits. These are the input electron gun, monochromator, the monochromator and analyzer deflectors, the lens systems, and the channeltron electron detector. The operation of this spectrometer is as follows. Electrons exit the electron gun, and after passing through the monochromator, they are focused onto the sample with the aid of the output zoom lenses. They are then scattered off the sample, and finally they pass through the analyzer and are collected by the channeltron.

In the electron gun, electrons are emitted from a tungsten hairpin "A"-shaped filament heated ~ 2000 °C. The filament is in the center of a repeller anode (R). After being focused by the repeller, the electrons are accelerated so that their energies are around a few tenths of an eV, and are focused by the three-element slit lens system (a_1 - a_3) into the monochromator entrance slit, whose size is $\sim 0.2\text{mm} \times 6\text{mm}$. The center axis along the slit is positioned at the mean radius of the pre-monochromator, where the potential should be the same as that of the slit (i.e., no potential step). After passing through the pre- and main monochromators, which are operated at ~ 0.5 eV pass energy, the highly monochromatized electrons are accelerated again, and focused onto the sample with the aid of a two-element lens system (e_1 and e_2). The sample is at the center of a grounded scattering box (F) and is kept at a potential which establishes a field-free region in this box. The actual electron primary energy is determined by the pass energy and the voltage drop between ground and the monochromator exit slit potential. On the sample surface, the electron beam current is typically $\sim 3 \times 10^{-10}$ A at ~ 7 meV energy.

After scattering off the sample and possibly suffering a loss of kinetic energy, the electrons leave the equipotential scattering region. They are then decelerated to few tenths of an eV (to achieve a high resolution) and focused onto the entrance slit of the pre-analyzer by the lenses e_3 and e_4 . After passing through the two stages of the analyzer, the electrons within the pass energy of the analyzer are collected by the channeltron electron detector and counted.

Comments on techniques

To obtain a high energy resolution, the pass energy for both the monochromator and analyzer must be reduced to 1 eV or less. This is because both the monochromator and analyzer elements are based on the 127° cylindrical deflector analyzer, whose base resolution ΔE_B is given by

$$\frac{\Delta E_B}{E_{pass}} = \frac{2s}{r} + \frac{4}{3}\alpha^2 + dh^2 \quad (2.1)$$

where E_{PASS} is the pass energy, r the mean radius, s and h , the slit width and height, respectively, α the maximum angular divergence of the entering electrons from the slit, and d a constant. The resolving power ($\Delta E_B/E_{PASS}$), determined by the analyzer geometry, is a constant. Therefore, to reduce ΔE_B , the pass energy E_{PASS} must be as low as possible. However, at an energy scale of few tenths of an eV, no matter which metal is chosen, the real surface potential can no longer be considered to be an equipotential, since the work function of a given metal can vary as much as 1 eV

across the surface. This variation can be caused by the surface orientation dependence of the work function, a patchy surface potential, and surface adsorption (i.e., contaminants), etc., even in an ultrahigh vacuum. As a result, random and uncontrolled electric fields will be present in the spectrometer, and operation at low energy will be impossible. To provide a uniform surface, a coating technique using graphite has been used on most HREELS spectrometers. The graphite is applied by a fine spray from an air brush, and baked at several hundred degrees centigrade.

Synchrotron Radiation Photoemission Spectroscopy

Synchrotron radiation photoemission spectroscopy uses the synchrotron radiation source to excite electrons in solids. The photoelectrons ejected out of surfaces have a specific kinetic energy determined by the photon energy and the energy level of the electrons when in the solid. Thus, the electron energy spectra yield a direct picture of the surface electronic structure. In addition, photoemission spectroscopy also yields information about the atomic structure of surfaces and interfaces.

Synchrotron radiation source

Electrons orbiting in a synchrotron are continuously accelerated towards the center of the orbit. According to electrodynamics, they emit radiation during

acceleration. Synchrotron radiation from the 800 MeV electron storage ring at the University of Wisconsin's Synchrotron Radiation Center (SRC) is used as the photon source for the photoemission experiments. The electron beam current is in the range of 60-160 mA. The greatest advantage inherent in this type of radiation source for use in photoemission spectroscopy is that the radiation has an intense continuum of photon energies which extends from the infra-red to the soft x-ray region. In addition, this radiation is highly collimated, polarized, and pulsed at a short wavelength.

Photon-energy monochromator

The monochromator used in the experiments is the Ames/Montana one; its optical layout is shown in Fig. 4. This monochromator is equipped with two grating systems. The yield in photon flux with respect to photon energy differs between the two gratings. The high energy grating (ERG) is most effective from 40-300 eV and was useful for measuring core level spectra, while the low energy grating (Seya) covers 4-40 eV and was most useful for valence band and Fermi-level measurements. These two systems can be switched *in vacuo*, allowing both valence band and high resolution core level photoemission studies to be conducted at the same time. The details of the ERG/Seya monochromator are reported by Olson.⁸² In addition, the entrance and exit slits are adjustable, permitting the user to optimize the flux/resolution factor for a given experiment.

Extended Rang Grasshopper - Seya Namioka Monochromators

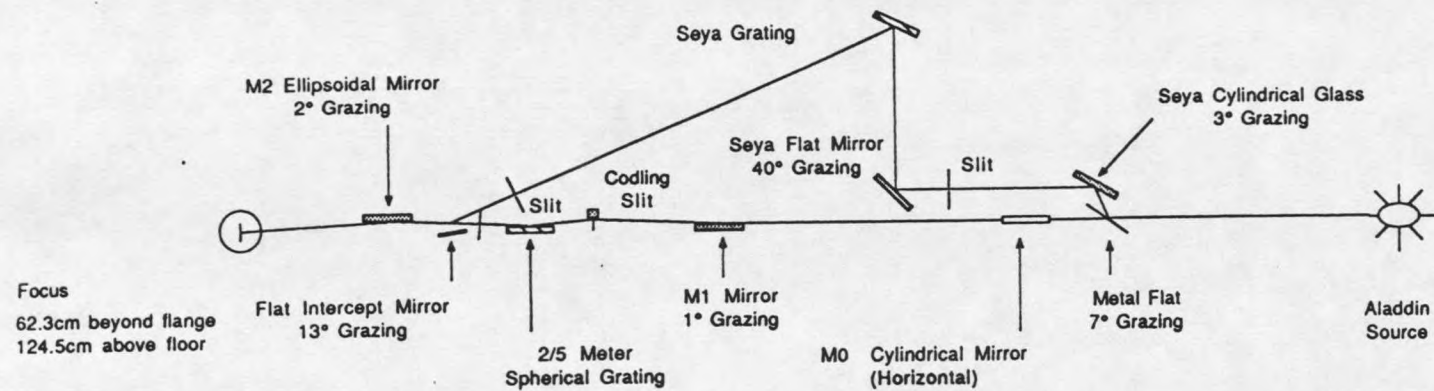


Fig. 4 Optical layout of Ames/Montana ERG/Seya monochromator.

Electron energy analyzer

The electron energy analyzer used in the photoemission experiments is the double-pass two-stage cylindrical mirror analyzer (CMA). This CMA, in contrast to ESCA/AES double-pass CMAs, has a unique feature, an angle-resolved drum within the inner cylinder. Figure 5 shows a schematic of the analyzer in two operation modes, the angle-integrated and angle-resolved modes. The trajectories for electrons through the analyzer are also indicated. In the angle-integrated mode, the analyzer functions as a normal double-pass CMA. In the angle-resolved mode, the drum is positioned between the iris of the first stage and the third set of slits, within the second stage inner cylinder. Therefore, the drum covers the slits, blocking all of the electron beam except that passed by the selected aperture on the cylindrical surface of the drum. By rotating the drum, any segment of the electron beam can be selected and passed through the second stage to be detected.

Sample Preparations

Doping density selection

Electron spectroscopy for surface analysis generally requires a conducting specimen, since sample charging is a problem that affects experimental results in many ways. For a semiconductor, a doped sample is required. In this thesis, the doping density even must satisfy additional stringent requirements, because it is

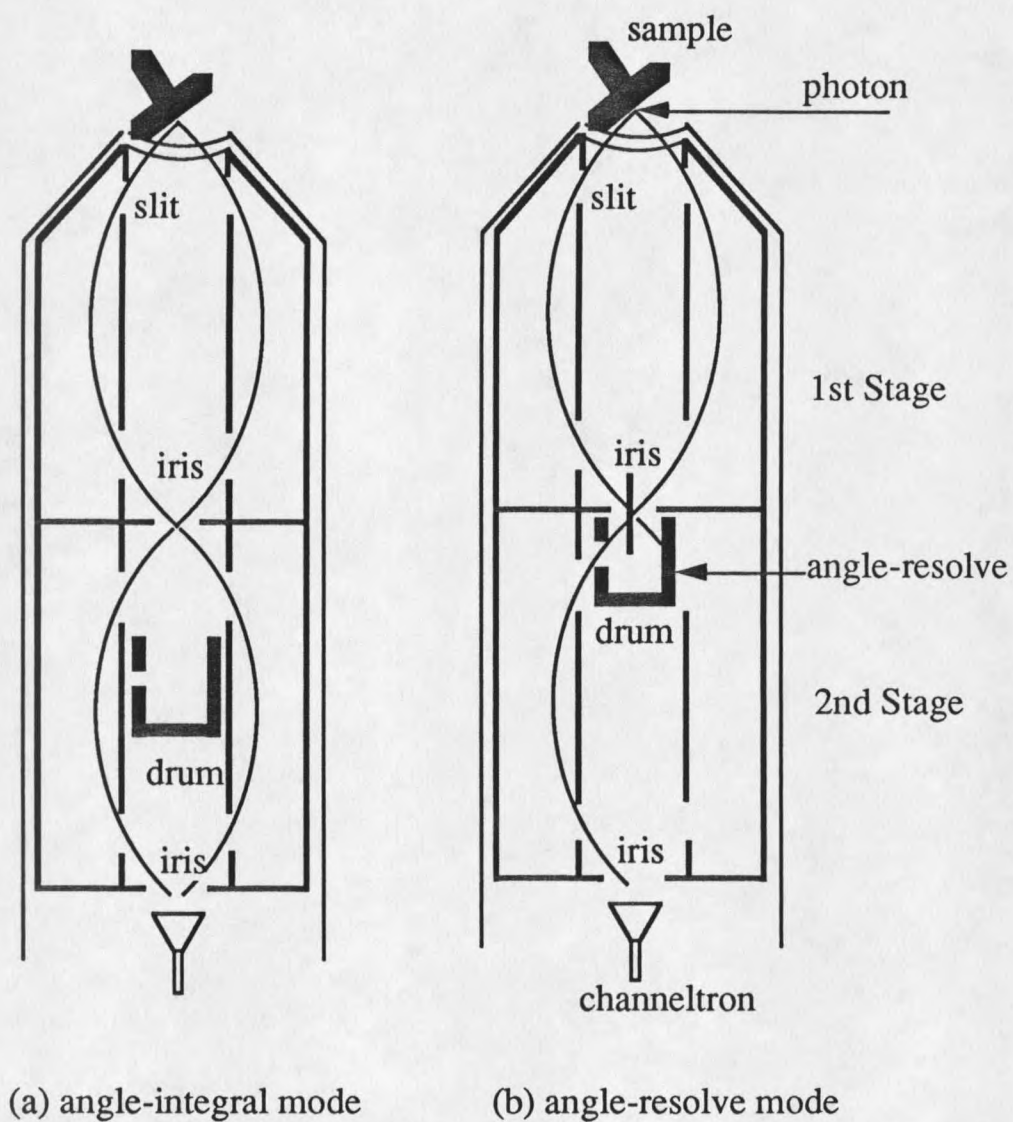


Fig. 5 Schematics of the angle-resolving double pass CMA. (a) In the angle integral mode. (b) In the angle resolving mode.

directly related to the experimental results, as we will discuss in following chapters. For the hole-plasmon excitation study, we select an extremely high doping density (Zn-doped, $>2 \times 10^{19} / \text{cm}^3$) in order to make the plasmon energy high enough to enable the loss feature to be seen above the background. For the Bi/InP(110) band bending study, a high doping density ($4 \times 10^{18} / \text{cm}^3$) for both n- and p-type InP is also selected, to avoid the photovoltaic effect.⁷⁸ For studies of overlayers on GaAs(110), the substrate doping density is $\sim 2.5 \times 10^{18} / \text{cm}^3$.

Clean sample preparations

Clean surfaces of GaAs(110) and InP(110) samples were prepared by the cleavage technique in ultrahigh vacuum. The cleaver consists of a tungsten-carbide blade with a 30° pitch and a flat anvil. The crystal is pressed between the blade and the anvil while the cleavage plane is parallel to the knife blade. In the low temperature experiments, the samples are cleaved when their temperature has been lowered and the chamber pressure has been reduced to $3\text{-}5 \times 10^{-11}$ Torr. The cleaved surfaces are examined with a telescope; the surfaces thus prepared for the measurements are smooth and flat.

Overlayer and H-adsorbed sample preparations

In the HREELS measurements, bismuth and ZnSe are evaporated from 1-2 mil Ta boats at a pressure of $<10^{-9}$ Torr in the measurement chamber which has an

operating base pressure of $<2 \times 10^{-10}$ Torr. In the photoemission measurements, bismuth is evaporated at $1\text{--}3 \times 10^{-10}$ Torr, and the chamber operating pressure is in the mid $\sim 10^{-11}$ Torr range. Evaporations are monitored with a quartz crystal oscillator (QCO). 1 ML is defined as 8.86×10^{14} atoms/cm² for GaAs(110) and 8.21×10^{14} atoms/cm² for InP(110), or two Bi atoms/unit mesh on the surface.

The hydrogen exposure was made with the sample surface in the line of sight of a hot (2200 K) tungsten filament, which is used to dissociate hydrogen molecules. The distance between the filament and the sample is ~ 5 cm. Dosing the samples with atomic hydrogen could result in the formation of a depletion layer on the surface. The hydrogen gas flows into the vacuum chamber through a leak valve which is capable of controlling the pressure in the low 10^{-9} Torr range. The exposure is recorded in Langmuirs ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr} \times \text{second}$).

CHAPTER III

PHOTOEMISSION MEASUREMENT AND DATA ANALYSIS

Synchrotron radiation photoemission spectroscopy has proved to be an extremely powerful technique for determination of the electronic properties and surface atomic structures of solids. However, this approach requires the proper handling of a series of operations, such as instrument setup, sample positioning, data acquisition, data analysis, etc.⁸³ In this chapter we focus on the interface structure and Fermi level studies, and discuss the measurement principle and the quantitative analysis of the data.

Principle of Measurement

Core-level measurement for interface studies

In one major application of the core-level studies, core-level photoemission spectroscopy is used as a local probe to determine the atomic structure of surfaces, adsorbates, and interfaces. When an ordered clean surface is created, the atoms in different layers near the surface sense different atomic environments.^{84,85} Thus, for

instance, the surface atoms may have core-level binding energies different from the corresponding bulk value (the difference in the binding energy is called the surface core-level shift). Core-level binding-energy shifts are also likely to occur for atoms near interfaces and for atoms within different layers in thin films. If these shifts can be resolved experimentally, one can then determine the relative numbers of atoms in surface or interface sites. With this information, structural models can be examined.

To resolve core-level shifts, one needs highly surface-sensitive data. By considering the photoemission process in which bound electrons absorb the photons and escape into the vacuum, we know that the photon-excited electrons finally collected by the analyzer are emitted from those atoms in a certain region below the surface. The width of this region is called the escape depth or the electron mean free path. This width depends only on the kinetic energy of the electrons, not on the individual atoms from which electrons are emitted, according to the universal escape curve.⁹¹ The width reaches a minimum at a kinetic energy around 50 eV, and the minimum value can be as small as 5 Å, i.e., one or two atomic layers. Using the relation $E_{\text{Kinetic}} \approx h\nu - E_{\text{Binding}}$, one can select the photon energy in such a way that the kinetic energy is in a specific region, say around 50 eV; the photoelectrons with this energy are emitted only from the minimum escape region, i.e., the most interesting region for surface studies.

We are able to select different photon energies for various core-levels (depending on the binding energy) by means of the synchrotron radiation source,

which provides a continuously tunable photon energy, so that the electron kinetic energy in turn is confined to a small range around 50 eV which corresponds to a surface sensitive region (4-5 Å). For instance, for the In 4d core level with a binding energy of ~17 eV, to obtain the electron kinetic energy of ~50 eV, a photon energy of 67 eV can be selected.

Measurement for Fermi-level study

In determining the character of the Fermi level in a semiconductor by means of photoemission, two major problems must be considered: one is the determination of the Fermi edge, the other one is the measurement of the Fermi level movement (i.e., band bending).

For semiconductor samples, the Fermi edge cannot be observed directly in the photoemission spectrum because the density of states at the Fermi level is essentially zero. In this case, the Fermi level position is usually determined by observing the Fermi edge emission from a metal sample (such as Cu) in electrical contact with the semiconductor.

The Fermi level movement (or band bending) can be obtained by observing the shifts in the kinetic energies of peaks originating from core levels with respect to the Fermi level of the metallic sample holder, if the kinetic energy of the core level emission is changed only due to the shift of the Fermi level at the surface.⁷³ However, for most cases, the kinetic energies of the core level emission from those atoms which

are in the surface sites (neighboring the vacuum) and the interface sites (neighboring overlayers), are also changed because of chemical reactions at the surface. These chemical shifts can be as large as a few eVs, whereas a typical semiconductor band gap is only 1-2 eV. Thus, the band bending has to be determined from the kinetic energy of the electrons emanating from bulk sites below the surface. The energy position of the bulk component can be obtained from a decomposition of the core level spectra. However this approach depends on the model used in the data analysis for the local surface structure. It is possible that an improper model can lead to a considerable error in the band bending results. One simple way to eliminate the uncertainty inherent in a specific structural model is to select the photon energy in a certain region so that the kinetic energy of the electrons is in the bulk-sensitive region (i.e., large escape length, 20 Å for 9 eV) according to the universal curve. In this instance, most of the photoelectrons which contribute to the core-level spectra are from atoms in bulk sites, so that the observed core-level spectrum, most likely, has only the bulk component.

Since the bulk sites in the depletion layer have different potentials, the kinetic energies of the electrons from these sites will be different, so the band bending result is an average over the escape depth region, rather than the edge of the depletion layer. Therefore, one may argue that the bulk-sensitive measurement is not of much value, since the escape length in this case is much larger than the surface-sensitive case. However, since the electron escape length (10-20 Å) is much smaller than a typical

value for the thickness of a depletion layer (200-1000 Å), the majority of ejected electrons could still be considered to come from the edge.

In addition, the photoemission technique itself can induce uncertainty into the band bending results, especially for the case of low temperature and low substrate doping density; this effect is due to the so-called photovoltaic effect. It is known that the band bending is due to depletion of carriers in a region near a semiconductor surface which may be from several hundred Å to several μm thick. A built-in electric field exists in this depletion region. In a photoemission experiment, when the photon beam, whose energy exceeds a threshold of the order of the semiconductor gap energy, shines on the surface, electron-hole pairs are created and are separated by this built-in field because of the opposite charge of electrons and holes. If the surface is not electrically grounded, an opposing voltage is produced. As a result, the original band bending is compensated by this photovoltage so that the measured value for band bending is reduced.

The photovoltage strongly depends on the doping density of the semiconductor and on temperature. This is because the electron-hole pairs created by photon absorption can be recombined by two major processes, tunneling and thermionic recombination. The former process is mainly controlled by the width of the depletion layer (i.e., the doping density). A small width (high doping) leads to a strong recombination so as to reduce the photovoltage. In the latter process, the temperature plays a key role. High temperature will significantly enhance the process. Therefore,

to minimize the photovoltaic effect in the band bending measurement, a high doped sample and high-temperature measurement are recommended, such as, $N_d > 10^{18} / \text{cm}^3$ and $T = 300 \text{ K}$.

In some cases, improper experimental procedures also result in some unexpected errors. It is strongly suggested that the photon energy be fixed in the band bending measurements. This is because changing the photon energy is accomplished by moving the gratings of the monochromator mechanically. Such a movement of the gratings sometimes may not be reproducible to a sufficient precision, which may lead to an uncertainty of the photon energy on the scale of several tenths of an eV.

Quantitative Analysis Procedures

Precise measurement is important in order to obtain a reliable experimental result for a physical quantity; however, in most cases, the precision is limited by such factors as instrument response, temperature, even the technique itself. Thus a quantitative analysis of experimental data is required. The procedure for quantitative analysis of photoemission energy distribution curves includes the determination of the background function, core-level lineshape, the Fermi level, etc. In this section, we outline the analysis procedures of the core-level and Fermi-level data.

Core-level data analysis

Background subtraction. The term background encompasses all signals present at a particular energy due to processes or sources other than those of primary interest. The background in energy distribution curves (EDCs) is due to the secondary electrons and the scattered electrons induced in the photoemission. The first step in an analysis procedure for core-level data is to remove this background mathematically from the EDCs. Nine methods of background subtraction have been developed so far, such as linear function, Shirley or integral function, etc. The one used in our studies for data analysis and core level fitting is a cubic polynomial function. In a background fitting routine, the first step is to match the intensity of the EDC and the derivative of the intensity of the EDC on each side of the core-level feature. Then the continuity condition allows one to obtain an inflection point of the background function near the centroid of the core feature when the background is relatively flat and not too near the secondary maximum. This inflection point and the matching of the intensity and slope at the endpoints gives a starting value for the background function.

Deconvolution. Our primary interest is in EDCs after background subtraction, which contain information on the core-level electron emission. However, since the electrons which contribute to the spectra come from many different electrical and chemical environments, the spectra actually contain the convolution of all of the individual core-level emissions. To deconvolute the spectra, one needs (1) a physical model of the surface structure, (2) the lineshape function for each core level.

The model for a particular surface or interface is first established on the basis of previous knowledge which comes from the general physical consideration and results of other measurements. The model can be modified during the fitting routine. For instance, for a clean surface, the two-component model, the surface component and bulk component, can be first considered. If the LEED observation indicates a surface reconstruction, another component can be added in the model.

The natural lineshape of a core level can be written as a Lorentzian of the form

$$L(E) = \frac{1}{(1 + 4(\frac{E - E_L}{\Gamma_L})^2)} \quad (3.1)$$

where E_L is the centroid and Γ_L is the full width at half maximum (FWHM). The Lorentzian width is independent of the probing photon energy, and does not change with coverages in the interface experiments. This width is normally obtained from the literature, or the clean-surface data fitting.

The instrument response function and the phonon broadening of the core level is represented by a Gaussian lineshape, which can be written as

$$G(E) = \exp[-4 \ln 2 (\frac{E - E_G}{\Gamma_G})^2] \quad (3.2)$$

where E_G is the Gaussian centroid and Γ_G is the FWHM. Γ_G is a function of both phonon broadening (which depends on the material under study, and temperature), and

the total instrument response which can be expressed as

$$\Delta E_{\text{instrument}} = [\Delta E_{\text{mono}}^2 + \Delta E_{\text{analyzer}}^2]^{1/2} \quad (3.3)$$

where ΔE_{mono} and $\Delta E_{\text{analyzer}}$ are the resolution functions for the monochromator and analyzer respectively.

The deconvolution process consists of fitting mathematical functions to the measured core-level EDC. The fitting function is a convolution of the Gaussian and Lorentzian functions. The parameters, i.e., width, centroid, etc. of the function and possibly the interface model are varied in order to achieve the best fit. The convolution can be expressed as the integral of the Gaussian function at E_G in the EDC with a Lorentzian at E_L

$$I(E_G) = \int \exp \left[-4 \ln 2 \left(\frac{E - E_G}{\Gamma_G} \right)^2 \right] \cdot \frac{1}{1 + 4 \left(\frac{E - E_L}{\Gamma_L} \right)^2} dE \quad (3.4)$$

Fermi-level determination

For a metal, the Fermi level is conventionally obtained by examining the high kinetic energy onset of the EDC to determine the energies at which the edge rises from 10% to 90% of the maximum value. E_F is then taken to be the center of these two points, and the energy difference is considered as the width of the Fermi cutoff. Here, the density of the states (DOS) near E_F is assumed to be a step function. A

more accurate determination of the Fermi level requires knowledge of the temperature dependent Fermi function, the DOS, and the instrument response function.

For a semiconductor, as we mentioned earlier, the Fermi edge can be determined by observing the Fermi edge emission from a metal sample in electrical contact with the semiconductor.

CHAPTER IV

BASIC THEORY OF HREELS

In this chapter we describe the interactions of the probing beam with surfaces. Since the theory of these interactions has been well documented, we present here the fundamental concepts and the related physical pictures, rather than a rigorous mathematic derivation. We then discuss several key issues in HREELS studies, such as the penetration depth, and the kinematical factor.

Theoretical Aspects

The theory of inelastic scattering of low-energy electrons was first established 30 years ago.^{3,5} Recently, it has developed rapidly within the framework of the so-called dielectric theory, where the electron is considered as a classical particle, while the collective excitations of the medium are described quantum mechanically.

An inelastic electron scattering process can be simply described as follows. When an electron approaches a surface, the Coulomb field of the moving electron penetrates into the surface to a frequency-dependent distance d . In this region, and the

medium is polarized, the polarization field from the dipoles of the substrate extending into the vacuum above the surface to the same distance d . Thus, when the electron travels through the region above the vacuum, it exchanges its energy and momentum with the polarization field. As a result, the scattered electron (here we treat only those electrons scattered in the specular direction), will have a different energy and momentum from the incident electron. These differences exhibit the signature of the surface excitations, through energy and momentum conservation.

Consider a slow electron with energy E_i and velocity $\vec{v}_e$ impinging on a surface as shown in Fig. 6. The (nonretarded) Coulomb potential in the vacuum ($z > 0$) generated by this moving electron is simply given by

$$\phi_{ext}(\vec{r}, t) = \frac{e}{|\vec{r} - \vec{r}_e(t)|} \quad (4.1)$$

This potential can be Fourier transformed with respect to coordinates parallel to the surface and the time t . For the case of $z < 0$ (i.e., within the surface), the result may be written as⁹²

$$\phi_{ext}(\vec{q}_{\parallel}, \omega, z) = -\frac{2\pi e}{q_{\parallel}} e^{q_{\parallel} z} \left[\frac{2q_{\parallel} v_{\perp}}{q_{\parallel}^2 v_{\perp}^2 + (\vec{q}_{\parallel} \cdot \vec{v}_{\parallel} - \omega)^2} \right] \quad (4.2)$$

where $\vec{q}_{\parallel}$ denotes a two-dimensional wave vector within the surface, and $v_{\perp}$ and $v_{\parallel}$ are the perpendicular and parallel components of the electron velocity, respectively. Eq. (4.2) illustrates that the Coulomb potential seen in the solid is a linear

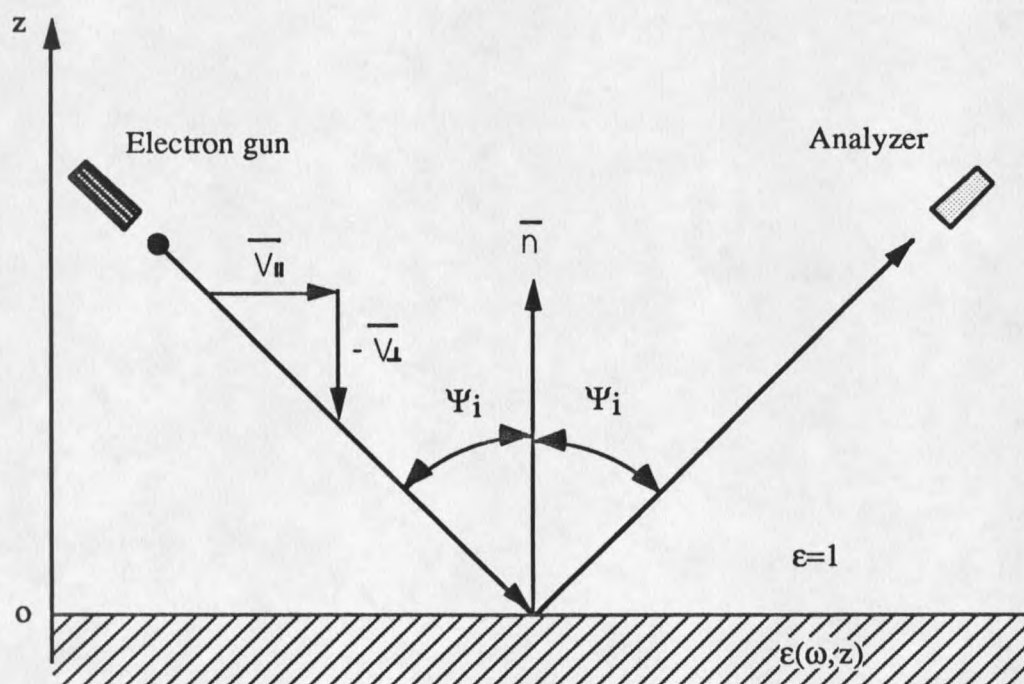


Fig. 6 HREELS principle and definition of the geometrical parameters.

combination of two-dimensional waves which penetrate into the solid a distance $l=1/q_{\parallel}$; for each ω (i.e., the mode frequency of those waves), the amplitude is proportional to a function $f(\vec{q}_{\parallel}, \omega)$ given by

$$f(\vec{q}_{\parallel}, \omega) = \frac{q_{\parallel} v_{\perp}}{[q_{\parallel}^2 v_{\perp}^2 + (\vec{q}_{\parallel} \cdot \vec{v}_{\parallel} - \omega)^2]} , \quad (4.3)$$

and has a maximum at

$$\omega = \vec{q}_{\parallel} \cdot \vec{v}_{\parallel} . \quad (4.4)$$

Eq. (4.4) will be used in the later discussion of the penetration depth of the probing electron.

The polarization field $\mathbf{E}(\vec{r}, t)$ is induced when the Coulomb field penetrates into the surface. This field can be determined in the framework of classical electrodynamic theory.⁹³ The work done by the polarization field $\mathbf{E}(\vec{r}, t)$ on the electron, computed along its classical trajectory, is written as

$$W = -e \int_{-\infty}^{\infty} \vec{v}_e \cdot \mathbf{E}(\vec{r}_e(t), t) dt , \quad (4.5)$$

where $\vec{r}_e(t)$ is the trajectory of the electron. For application to HREELS studies, it is useful to transform $\vec{v}_e$ and $\mathbf{E}(\vec{r}, t)$ in Eq. (4.5) with respect to the coordinates parallel to the surface and the time t . Thus, the work can be reexpressed in the form

$$W = \int_0^{\infty} d\omega \, \hbar\omega P_{loss}(\omega), \quad (4.6)$$

where $P_{loss}(\omega)$, the probability per unit frequency that the electron has lost the energy $\hbar\omega$, is given by the following expression⁶

$$P_{loss}(\omega) = \text{Im} \left[\frac{-4ev_{\perp}}{\hbar} \int \frac{d^2q_{\parallel} E_{\perp}(\vec{q}_{\parallel}, \omega, +0)}{[(v_{\perp} q_{\parallel})^2 + (\omega - \vec{v}_{\parallel} \cdot \vec{q}_{\parallel})^2]} \right]. \quad (4.7)$$

Here $E_{\perp}(\vec{q}_{\parallel}, \omega, +0)$ is the normal component of the Fourier transform of the polarization field just above the surface.

In Eq. (4.7) we see that the loss probability $P_{loss}(\omega)$ is mainly determined by $E_{\perp}(\vec{q}_{\parallel}, \omega, +0)$, the polarization field at the surface; whereas $E_{\perp}(\vec{q}_{\parallel}, \omega, +0)$ is determined by the external Coulomb field at the surface and the dielectric properties of the material, as we will show below.

The electric field above the surface ($z > 0$) is the sum of the polarization field and the Coulomb field of the electron. The boundary condition at the surface (continuity of the normal component of $\mathbf{D}$), gives

$$E_{\perp}(\vec{q}_{\parallel}, \omega, +0) + E_{e\perp}(\vec{q}_{\parallel}, \omega, 0) = D_{\perp}(\vec{q}_{\parallel}, \omega, -0) \quad (4.8)$$

where $+0$ and -0 , represent positions just above and below the surface, and

$E_{e\perp}(\vec{q}_{\parallel}, \omega, 0)$ is the normal component of the Fourier transform of the Coulomb field at the surface. Eq. (4.8) shows that $E_{\perp}(\vec{q}_{\parallel}, \omega, +0)$ can be solved if $D_{\perp}(\vec{q}_{\parallel}, \omega, -0)$ is

known.

Below the surface, the field $\mathbf{E}(\vec{r}, t)$ satisfies $\nabla \times \mathbf{E} = 0$ and $\nabla \cdot \epsilon \mathbf{E} = 0$. In terms of the Fourier transform of $\mathbf{E}(\vec{r}, t)$, these two Maxwell equations lead to the following quantity which was introduced by Lambin⁶

$$\xi(\vec{q}_{\parallel}, \omega, z) = i \frac{D_{\perp}(\vec{q}_{\parallel}, \omega, z)}{E_{\parallel}(\vec{q}_{\parallel}, \omega, z) \cdot \vec{q}_{\parallel} / q} \quad (4.9)$$

with $D(\vec{q}_{\parallel}, \omega, z) = \epsilon(\omega, z) E(\vec{q}_{\parallel}, \omega, z)$, where $\epsilon(\omega, z)$ is the long-wavelength dielectric constant of the material, and $\xi(\vec{q}_{\parallel}, \omega, z)$ is called the effective dielectric function of the material. Eq. (4.9) provides a bridge between $D_{\perp}(\vec{q}_{\parallel}, \omega, -0)$ and those parallel components of the polarization field which can be obtained from the parallel boundary conditions. Thus, one can write Eq. (4.8) as

$$(1 + \xi_0) E_{\perp}(\vec{q}_{\parallel}, \omega, +0) = -i \xi_0 \vec{q} \cdot \mathbf{E}_{\parallel}(\vec{q}_{\parallel}, \omega, 0) / q - E_{\perp}(\vec{q}_{\parallel}, \omega, 0) \quad (4.10)$$

where ξ_0 is a short-hand notation for $\xi(\vec{q}_{\parallel}, \omega, -0)$.

Eq. (4.10) shows, for the case where the external field is absent, that the polarization field in the vacuum vanishes, unless the following condition is fulfilled:

$$\xi_0 = \xi(\vec{q}_{\parallel}, \omega, 0) = -1 \quad (4.11)$$

The regions of $\vec{q}_{\parallel}$ and ω given by (4.11) correspond to the electromagnetic eigenmodes of the material.

Replacing $E_{\perp}(\vec{q}_{\parallel}, \omega, +0)$ by its expression deduced by Eq. (4.10), one arrives at the following result:

$$P_{loss}(\omega) = \frac{2e^2}{\pi\hbar^2 v_{\perp}} \int_D \frac{d^2 q_{\parallel} (q_{\parallel} v_{\perp})^3}{q_{\parallel}^2 [(\mathbf{v}_{\perp} \cdot \mathbf{q}_{\parallel})^2 + (\omega - \mathbf{v}_{\parallel} \cdot \mathbf{q}_{\parallel})^2]^2} \times P(\vec{q}_{\parallel}, \omega). \quad (4.12)$$

where the integration is performed over a domain D including all surface wave-vectors $\vec{q}_{\parallel}$ which, through energy and momentum conservation, scatter the reflected electron towards the detector aperture.

In Eq. (4.12) we have introduced the energy-loss function $P(\vec{q}_{\parallel}, \omega)$, which is defined by

$$P(\vec{q}_{\parallel}, \omega) = \frac{2\hbar}{\pi} \text{Im} \frac{-1}{\xi_0(\vec{q}_{\parallel}, \omega) + 1} \quad (4.13)$$

Eq. (4.12) illustrates that the loss probability for the inelastic scattering process is determined by both the material properties (the loss function) and the probing electron behavior (the kinematical factor which we discuss in the next section).

The loss function given by Eq. (4.13) reflects the dielectric response of the material which is described by $\xi_0(\vec{q}_{\parallel}, \omega)$, the effective dielectric function of the material at the surface defined by Eq. (4.9). For isotropic media, $\xi_0(\vec{q}_{\parallel}, \omega)$ generally can be found from the Riccati equation.⁶ For the case of a semi-infinite isotropic medium with $\epsilon(\omega)$, it is given that $\xi_0(q_{\parallel}, \omega) = \epsilon(\omega)$, which shows that $\xi_0(\vec{q}_{\parallel}, \omega)$ reduces to the dielectric constant $\epsilon(\omega)$ of the medium. In this case, the eigenmode given by Eq. (4.11) is the well known surface mode. (Actually, this is the reason why ξ_0 is called the effective dielectric function). Eq. (4.11) therefore can be considered

as a generalization of the well-known condition $\epsilon(\omega)=-1$.

For heterogeneous materials consisting of a succession of layers with parallel interfaces, ξ_0 is given by

$$\xi_0(q_{\parallel}, \omega) = a_1 - \frac{b_1^2}{a_1 + a_2 - \frac{b_2^2}{a_2 + a_3 - \frac{b_3^2}{a_3 + a_4 - \dots}}} \quad (4.14)$$

where $a_i = \epsilon_i(\omega) \coth(q_{\parallel} d_i)$, $b_i = \epsilon_i(\omega) / \sinh(q_{\parallel} d_i)$, d_i and ϵ_i are the thickness and dielectric constant of the i th layer.

Eq. (4.14) will be considered as the formal basis for this thesis and will be applied to all the layered structure problems in the following chapters.

Further Discussion

Having established a general description of the basic process for HREELS, where the probing electrons are scattered inelastically by the surface, we now present some comments on several key issues in the HREELS study, such as the penetration depth of the field of the moving electron, and the kinematical factor, which will play a central role in our discussions.

Penetration depth

As mentioned above, the external electric field of the probing electron is synthesized from a linear combination of two-dimensional waves, each of which is localized near the surface and penetrates into the surface a distance of about $l=1/q_{\parallel}$, as Eq. (4.2) illustrates. On the other hand, the amplitudes for those two-dimensional waves are proportional to $f(\vec{q}_{\parallel}, \omega)$, given by Eq. (4.3). For specified values of ω and $\vec{v}$, only those two-dimensional waves whose wave vectors fulfill (or nearly fulfill) Eq. (4.4) dominate the whole field, because of the resonance-type expression for $f(\vec{q}_{\parallel}, \omega)$ (in fact, it is a δ -function of $q_{\parallel}$ at the limit that $q_{\parallel}v_{\perp} \rightarrow 0$). Thus, the penetration depth of the external field (the Coulomb field) can be evaluated by Eq. (4.4). That is,

$$l = \frac{1}{q_{\parallel}} \sim \frac{v_{\perp}}{\omega} \sim \frac{\sqrt{E_I}}{\omega} . \quad (4.15)$$

This result illustrates how the penetration depth varies with the primary energy of the probing electron: with higher primary energy, the probing electron penetrates farther into the surface. In addition, it also shows that excitations (e.g., interface excitations) with lower energy can be more easily observed. Using this result, we can study the spatial distributions of the interface excitations by changing the primary energy; this will be discussed in the later chapters.

Kinematical factor

To better understand the kinematical factor and its effect on the loss probability function (i.e., the loss spectrum), we make the simplifying assumption that the sample material is isotropic, i.e., the loss function depends only on the magnitude and not on the direction of $q_{\parallel}$. The two-dimensional $q_{\parallel}$ integration in Eq. (4.12) can then be simplified to a one-dimensional expression:

$$P_{loss}(\omega) = \frac{2e^2 v_{\perp}^2}{\pi \hbar^2} \int_0^{q_{max}} dq_{\parallel} K(q_{\parallel}, \omega) P(q_{\parallel}, \omega), \quad (4.16)$$

where q_{max} is chosen to correspond to the finite aperture angle of the spectrometer in the experiments and is determined from $q_{max} = k_I \Delta\theta$, where $\Delta\theta$ is the half width of the angular aperture of the spectrometer, k_I the wave vector of the probing electron, and $P(q_{\parallel}, \omega)$ is the so-called loss function given by Eq. (4.13).

$K(q_{\parallel}, \omega)$ in Eq. (4.16) is defined by

$$K(q_{\parallel}, \omega) = q_{\parallel}^2 \int_0^{2\pi} d\theta \frac{1}{[(v_{\perp} q_{\parallel})^2 + (\omega - v_{\parallel} q_{\parallel} \cos\theta)^2]^2}. \quad (4.17)$$

and is called the **kinematical factor**, since it describes only the kinematics of the probing electron, not the response of the medium. The analytic result for the angular integration in Eq. (4.17) is given elsewhere.²⁰ Numerical calculations of the kinematical factor show that it is a resonance-type function of ω . Its peak position, FWHM, and its amplitude are determined by the electron velocity (i.e., the primary

energy) and $q_{\parallel}$. For a low primary energy and small $q_{\parallel}$, its amplitude is relatively large, a sharp resonance peak appears at very low ω (this is why, in the low-primary-energy experiments, the background near the elastic peak is higher than that in the higher primary-energy case); for a large $q_{\parallel}$ (e.g., $q_{\parallel} \sim q_{\max}$) and larger primary energy, the peak is broadened and the amplitude is small, and the resonance peak appears at high ω (if the resonance feature is not smeared out). To evaluate the overall influence of the kinematical factor on the loss probability function, however, one has to carry out an integration of $K(q_{\parallel}, \omega)$ over $q_{\parallel}$, as Eq. (4.17) illustrates. We consider here a simple case where the loss function given by Eq. (4.13) depends only on ω corresponding to the case of a semi-infinite uniform medium, so that $P_{\text{loss}}(\omega)$ now becomes

$$P_{\text{loss}}(\omega) = \frac{2e^2 v_{\perp}^2}{\pi \hbar^2} P(\omega) \int_0^{q_{\max}} dq_{\parallel} K(q_{\parallel}, \omega) . \quad (4.18)$$

where the integration of $K(q_{\parallel}, \omega)$ over $q_{\parallel}$ has been found to be proportional to $1/\omega$.⁴ For this specific case, the overall effect (i.e., after the integration) of the kinematical factor on $P_{\text{loss}}(\omega)$ does not contribute to a sharp resonance (this, perhaps, is why no observed loss features can be attributed solely to the kinematical factor). However the function $1/\omega$ can sometimes significantly modify the features observed in the loss function. In the next chapter, we will present example of this.

CHAPTER V

HOLE-PLASMON EXCITATION

In this chapter we study the valence-band hole-plasmon excitations in p-GaAs and their associated dielectric responses. First, we present the HREELS observation of the surface hole plasmon, and a quantitative analysis using the dielectric theory. Next, we discuss an interesting temperature effect observed in the loss spectra of heavily doped p-GaAs(110), and show that this effect is due to the temperature dependence of the carrier scattering process. We demonstrate that the valence-band hole plasmon has similar properties to the conduction-band electron plasmon, except that the holes have significantly larger scattering cross sections, leading to strong damping of the external excitation. Finally, we study the hole-plasmon behavior for the case where a depletion layer is present near the surface.

Introduction

The surface excitations of GaAs(110) were first studied by Matz and Lüth using HREELS.¹ They observed the conduction-band electron plasmon on a cleaved

n-GaAs(110) surface. For the sample with a doping level of $3 \times 10^{17} / \text{cm}^3$, the surface plasmon mode is found at ~ 20 meV, and the Fuchs-Kliwer phonon mode at ~ 36 meV. The experimental result was consistent with their theoretical prediction.¹ Recently, Chen *et al.*,¹⁰ studied this system in more detail. Using a high resolution (5 meV) and an intermediate doping level ($1.3 \times 10^{18} / \text{cm}^3$), they observed the coupling between the phonon and plasmon. In addition, they successfully described the experiments with a model using the framework of local-response dielectric theory and found that the Thomas-Fermi and the Debye-Hückel dielectric models, which approximate the Lindhard dielectric function by using a quadratic q dependence, yield spectra that agree reasonably well with the full theory.

In contrast to many studies of the electron plasmon, the study of the valence-band hole plasmon is only in its beginning stages. For p-type GaAs, there are two p-like degenerate bands at the top of its valence band. Because of their different band curvature the holes in these bands have different effective masses: m_{LH}^* ($0.082 m_e$) for light holes and m_{HH}^* ($0.45 m_e$) for heavy hole, where m_e is the free electron rest mass.⁸⁰ Since the density of states for the two bands is proportional to $(m^*)^{3/2}$ (Ref. 78), and the Fermi level is at the same position for both bands, the densities for light and heavy holes, n_{LH} and n_{HH} , can be easily found to be 7.2 and 92.8 percent of the total density n_{H} , respectively.

Egdell *et al.* calculated the surface light- and heavy-hole plasmon energies for p-GaAs(110), using the well-known formula for the surface-plasmon frequency⁴

$$\omega_{SP} = \sqrt{\frac{4\pi n e^2}{m^*(\epsilon_{\infty} + 1)}} \quad (5.1)$$

where ϵ_{∞} is the high-frequency dielectric constant, n and m^* are the density and the effective mass for carriers. They found that when the total doping density is $1 \times 10^{19}/\text{cm}^3$, the surface light-hole plasmon energy is ~ 31.6 meV, and the heavy-hole plasmon is at the higher energy of 49.8 meV. They also calculated the plasmon frequency for the case where a GaAs depletion layer is formed on top of the bulk substrate by a two layer model (this frequency can be obtained from Eq. (4.11)). They found that the frequency varies with the depletion layer thickness d , in a certain region, from the surface-plasmon frequency given by Eq. (5.1) to the interface-limit frequency ($d \rightarrow \infty$) given by

$$\omega_{IP} = \sqrt{\frac{4\pi n e^2}{m^*(\epsilon_{\infty} + \epsilon_{\infty})}} \quad (5.2)$$

In the interface limit, the frequencies are 22.4 meV for the light holes, and 35.4 meV for the heavy holes. The electron-plasmon studies show that a strong coupling between the plasmon and the phonon modes takes place if their energies are close to each other. Therefore, Egde *et al.* expected that the strong coupling between the optical phonon and light- and heavy-hole plasmons should also be observed, since at least one of those hole plasmon energies is quite close to the phonon energy, independent of the depletion layer which may be formed during the sample

preparation. However, not only were they unable to observe the coupling, but they were unable to resolve the expected loss peaks due to the hole plasmon. It was unclear at that time that whether this result was due to some unknown technical problems or the intrinsic complexity of the loss function for p-GaAs.

Surface-Hole Plasmon

Observation

A typical HREELS spectrum of a heavily doped p-type GaAs(110) fresh-cleaved sample obtained at a temperature of 80 K is shown in Fig. 7. Here, in order to separate the hole-plasmon loss peak from the phonon peak and the inelastic background, we chose extremely heavy doping ($2.2 \times 10^{19} / \text{cm}^3$). In Table I, we list the values relevant to the surface hole plasmon for this doping density and for the doping density used in Ref. 7 ($1.0 \times 10^{19} / \text{cm}^3$) as well. Low temperature is found to be very helpful for the observation for reasons discussed below.

The spectrum clearly shows a well defined peak with peak position at 75 meV and a width of ~ 60 meV. Fig. 7 shows that only one plasmon peak is observed with peak position at 75 meV, which is higher than that expected for either the light- or heavy-hole surface plasmon energy.

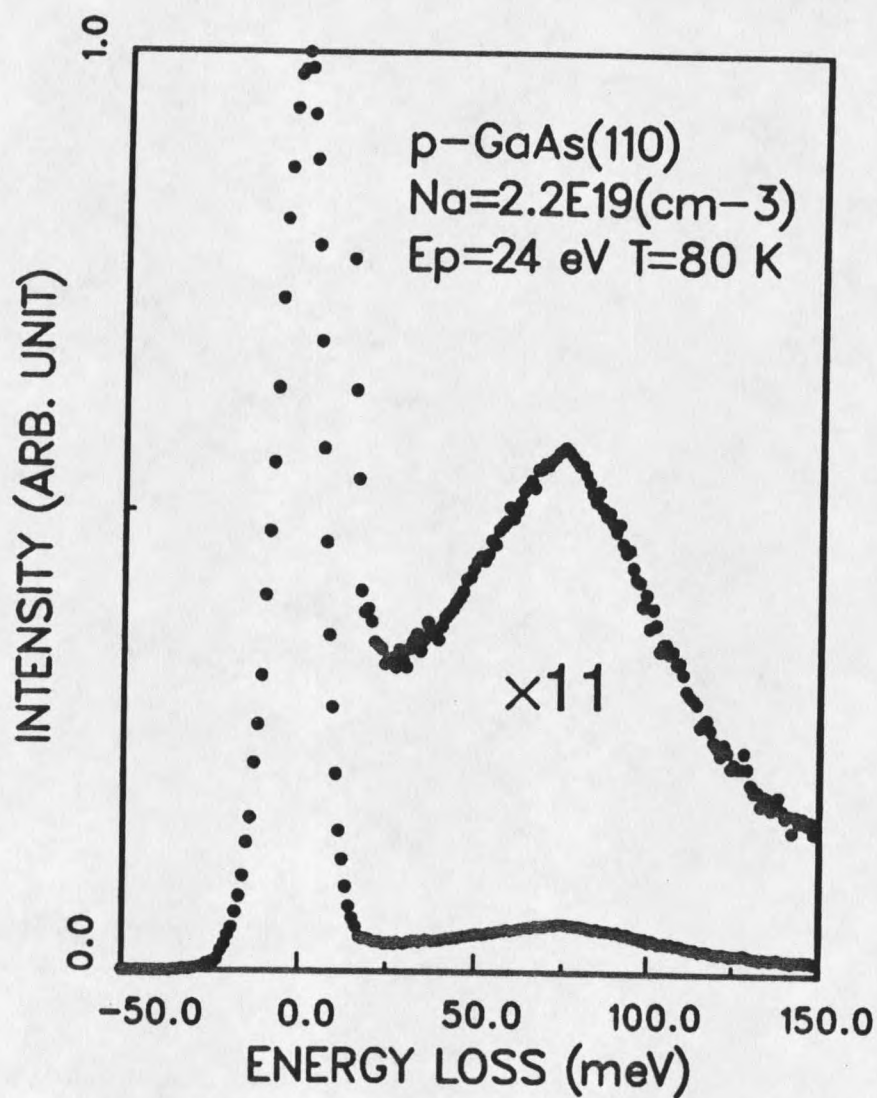


Fig. 7 A HREELS spectrum of a fresh-cleaved p-type (Zn-doped, $2.2 \times 10^{19} / \text{cm}^3$) GaAs(110) surface, measured at 80 K

Table I The values relevant to the surface hole plasmon for two different doping densities

	n_{th} (cm^{-3})	m_l^* (m_e)	m_h^* (m_e)	m_{σ}^* (m_e)	n_{lh} (n_{th})	n_{hh} (n_{th})	ω_{slh} (meV)	ω_{shh} (meV)	ω_{sep} (meV)
Our case	2.2×10^{19}	0.082	0.45	0.34	7.2%	92.8%	47.3	72.5	86.5
Ref. 7	1.0×10^{19}	0.082	0.45	-	7.2%	92.8%	31.6	49.8	-

m_e : free electron rest mass

m_l^* : light hole effective mass

m_h^* : heavy hole effective mass

m_{σ}^* : conductivity hole effective mass

n_{lh} : light hole density

n_{hh} : heavy hole density

n_{th} : total hole density

ω_{slh} : surface light hole plasmon energy

ω_{shh} : surface heavy hole plasmon energy

ω_{sep} : equivalent surface hole plasmon energy

Equivalent hole plasmon

If we consider the Drude model (ignoring the damping term), the contribution of the light- and heavy-hole plasmas to the dielectric function is given by

$$\chi(\omega) = \chi_{LH}(\omega) + \chi_{HH}(\omega) = -\frac{4\pi n_{LH} e^2}{m_{LH}^* \omega^2} - \frac{4\pi n_{HH} e^2}{m_{HH}^* \omega^2} \quad (5.3)$$

If we combine these two terms, we have

$$\chi(\omega) = -\frac{4\pi n_H e^2}{m_\sigma^* \omega^2} = -\frac{\omega_{EP}^2}{\omega^2} \quad (5.4)$$

where ω_{EP} is the equivalent hole plasmon energy, and m_σ^* is the equivalent effective mass given by

$$\frac{1}{m_\sigma^*} = \frac{n_{LH}}{n_H m_{LH}^*} + \frac{n_{HH}}{n_H m_{HH}^*} \quad (5.5)$$

From Eqs. (5.3) and (5.4), we can see that within the Drude model the effect of the combined light- and heavy-hole plasmas could be considered as that of a single equivalent hole plasmon in the dielectric function, the energy of the equivalent hole plasmon being higher than that of either light or heavy holes. Thus it is not surprising that only one plasmon (the equivalent plasmon) is observed in the HREELS spectrum. The equivalent surface hole plasmon energy, given by Eq. (5.1), is 86 meV. Note that, the observed peak position of 75 meV is lower than the value of 86 meV, a reason

for this discrepancy is discussed below.

The joint effect of both light-holes and heavy-holes on the dielectric function can be understood as follows. In the absence of collisions the equation of motion of a hole in an electric field E is $m_h \frac{d^2x}{dt^2} = eE$. If x and E have the time dependence of $e^{-i\omega t}$, the equation becomes $-\omega^2 m_h x = eE$. The dipole moment p of this hole is $p = ex = -e^2 E / m_h \omega^2$, and the polarization, defined as the **sum** of all the dipole moments per unit volume, is

$$P = n_{HH} ex + n_{LH} ex = \left(\frac{n_{HH} e^2}{m_{HH}^* \omega^2} + \frac{n_{LH} e^2}{m_{LH}^* \omega^2} \right) E \quad (5.6)$$

which leads to Eq. (5.4) by the definition of the dielectric function.

Discussion of the peak width

Figure 7 also shows that the width of the surface hole plasmon is large, ~ 60 meV for holes, compared with 10 meV for electrons.¹⁰ Generally, the lineshape of a surface plasmon depends on free carrier properties such as the plasmon dispersion, the density distribution, etc. To study these effects for a degenerate semiconductor material, it is necessary to treat the system as a nonlocal dielectric, and the carrier density and surface potential must be obtained self-consistently.²¹ However, Xu and Hermanson²⁴ have compared the calculated dispersion relation of surface plasmons using both local and nonlocal response for an n-type GaAs system, and have shown

that local dielectric response models still can provide a qualitatively correct description in doped semiconductors at long wavelength.

Thus, for p-type GaAs clean surfaces, a simple model composed of vacuum and the GaAs substrate is used, based on the previously discussed theory. Three approximations of the dielectric function, i.e. Drude, Thomas-Fermi, and Debye-Hückel, have been considered in the local dielectric function in order to estimate the influence of the surface-plasmon dispersion on HREELS. The energy-loss probability is given by the product of a kinematical factor and the surface loss function $\text{Im}(-1/(1+\epsilon(\omega, q)))$,⁴ where the complex dielectric function $\epsilon(\omega, q)$ is²⁴

$$\epsilon(q, \omega) = \epsilon_{\infty} + \chi_{\text{phonon}} - \frac{4\pi n_H e^2}{m_{\sigma}^* (\omega^2 + i\omega\Gamma - DR(q))} \quad (5.7)$$

where Γ is the damping term, χ_{phonon} is the optical phonon contribution to the dielectric function, and $DR(q)$ is the hole-plasmon dispersion term and is equal to zero, $3q^2 v_F^2/5$, and $3q^2 k_B T/m_{\sigma}^*$ for the Drude, Thomas-Fermi, and Debye Hückel dielectric models, respectively.

First, we consider the Drude model, which ignores dispersion. The resultant spectrum A in Fig. 8 shows the calculated results obtained by adjusting the damping term Γ to fit the experimental data; Γ is about 64 meV. As a check, we estimate Γ from the hole bulk mobility μ (70 cm²/V sec) using the Drude relaxation time $\tau = 1/\Gamma = m_{\sigma}^* \mu / e$, and find it is about 44 meV. Thus, the results indicate that the large

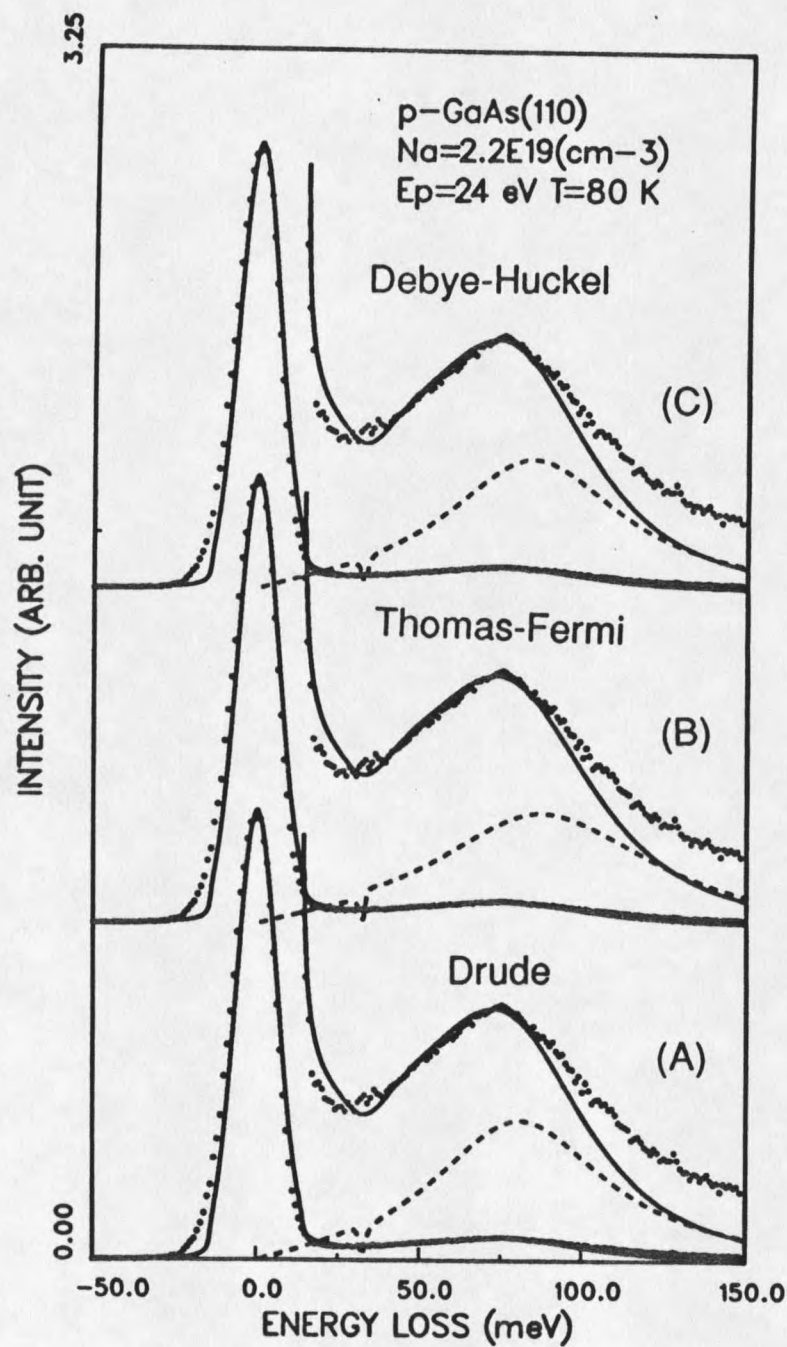


Fig. 8 The calculated HREELS spectra (solid curves) for three approximation of the dielectric function, i.e., Drude, Thomas-Fermi, and Debye-Hückel. The dashed curves show the q -integrated loss function.

peak width is due to the scattering rate determined by the hole mobility. The difference between these two Γ 's might be due to the simplicity of the model or/and the lower surface mobility. Both of these values are significantly larger than 10 meV, the typical value of the electron plasmon peak width for heavily doped n-GaAs, because the hole mobility is lower than the electron mobility. Further, we estimate the effect of the dispersion term by considering the Thomas-Fermi, and Debye Hückel models. The calculated loss spectra for the latter models are shown in Fig. 8 (B and C) with a Γ of 64 meV. However, one can see no significant difference between these two spectra and the Drude spectrum, which indicates that the surface dispersion has no significant effect on HREELS spectra. The calculation has also been carried out with the same parameters as above except for a Γ of 10 meV, and we still find essentially no difference among the calculations for the three dispersion models. Thus, we conclude that the large surface hole plasmon peak width is due to the low hole mobility rather than the hole plasmon dispersion at our high doping levels.

Effect of kinematical factor

Another interesting feature in Fig. 7 is that the observed hole plasmon peak position (~ 75 meV) is not the same as the surface equivalent hole plasmon energy ω_{sp} (~ 86 meV) given by Eq. (5.1). This is because the calculated spectra depend not only on the loss function, but also the kinematical factor. For the case that the loss function is independent of wave vector $\mathbf{q}$ (the Drude model), the frequency dependence of the

kinematical factor can be described approximately by $1/\omega$,⁴ and the loss peak position is given by

$$\omega_{pp} = \sqrt{\omega_{sp}^2 - \frac{\Gamma^2}{2}} \quad (5.8)$$

where ω_{sp} is the surface plasmon energy, Γ is the scattering rate, and ω_{pp} is the observed peak position. For a typical n-type GaAs system, Γ is ~ 10 meV, so ω_{pp} is 85.7 meV when ω_{sp} is 86 meV. Thus the kinematical factor has almost no effect on the loss-peak position. On the other hand, for a typical p-type system, Γ is ~ 60 meV, and ω_{pp} becomes 74.8 meV rather than 86 meV. In Fig. 8, we plot the q-integrated loss functions (the dashed curves) to illustrate the significant influence of the kinematical factor on the loss spectra. Thus, Eq. (5.7) implies that the kinematical factor must be taken into account in the HREELS calculations if the scattering rate is comparable to the surface-plasmon energy, e.g. in p-GaAs.

Temperature Effect

Observation

Figure 9 shows HREELS spectra of a heavily doped p-GaAs(110) clean surface taken over a closed temperature cycle. The spectrum A was taken just after the sample surface was obtained by cleavage at ~ 80 K (within a few minutes). Then

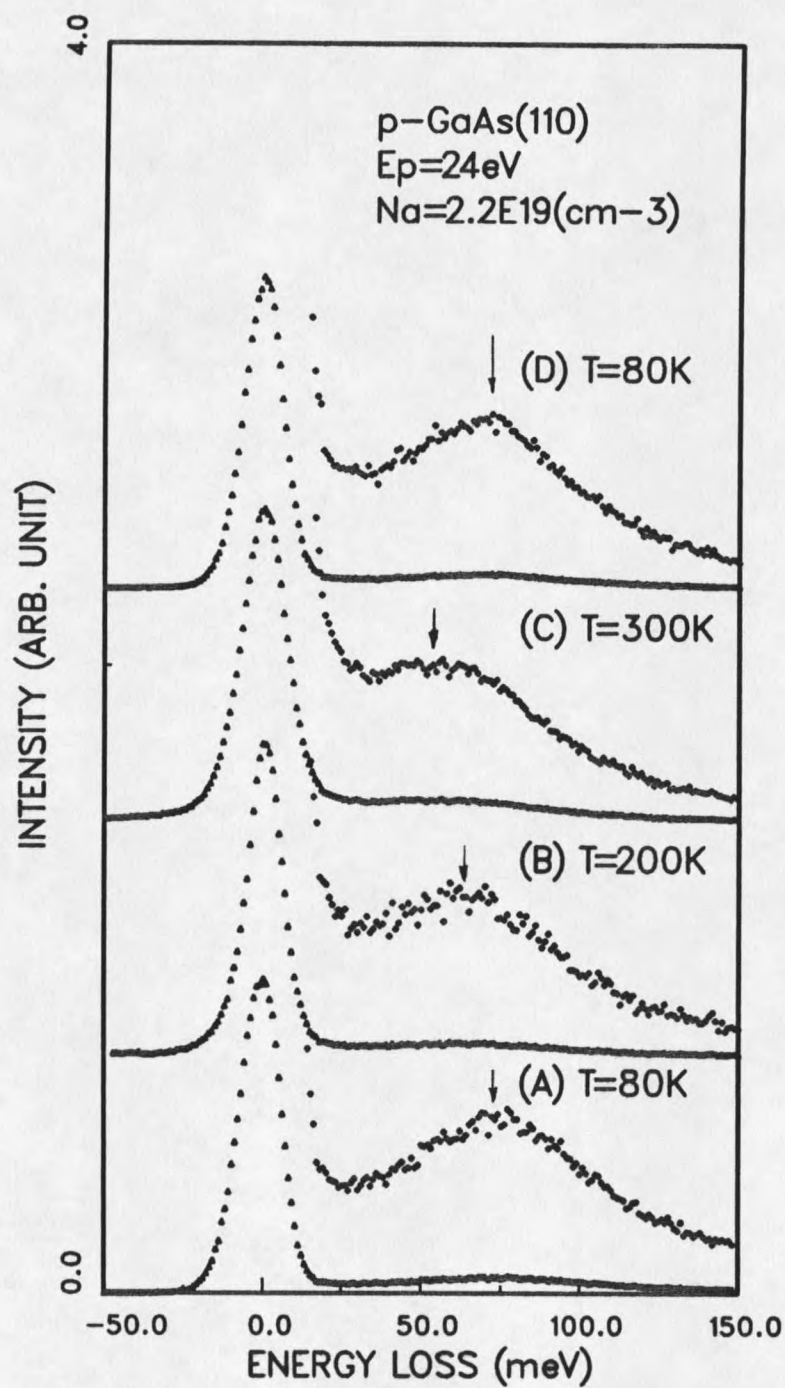


Fig. 9 Temperature dependent HREELS spectra for a clean heavily doped p-GaAs(110) surface taken in a cyclic manner (A→B→C→D).

the sample was warmed, and spectrum B was taken at 200 K, and spectrum C at 300 K. Finally we cooled the sample back to 80 K and took spectrum D. Several features of the hole plasmon peak can be clearly found in Fig. 9. (1) The low-temperature spectra (A and D) show a single well-defined hole-plasmon peak at energy of 75 meV, and this plasmon peak becomes broader with increasing temperature as shown by spectra B and C. (2) The plasmon peak position shifts to lower energy with temperature. (3) This temperature dependence of the plasmon peak is reversible, which rules out the possibility that the peak shifting with temperature might be due to the surface contamination during the temperature cycle.

Commentary

The temperature dependence of n-type semiconductor surface plasmons has been studied with HREELS by several authors.^{13,22,23} It was found that on Si(111) and undoped or lightly doped n-GaAs(100) surfaces, the surface-plasmon resonance loss features which lie in the elastic peak change with temperature because of the thermal activation of carriers across the gap which changes the elastic peak width. For a heavily doped n-GaAs(110) surface, the surface plasmon peak was nearly independent of temperature in a certain temperature range (50-300 K); i.e., neither the peak position nor the width changes with the temperature,²² since the number of electrons being thermally activated across the gap is negligible compared to those from the donors. The question naturally arises as to the mechanism of which can only be

observed in the p-type spectra, not in the n-type. If as the n-type study suggested, the thermal activation of free carriers can be neglected, why does the hole plasmon peak shift with temperature ?

Data analysis

Three calculated HREELS spectra, with various values of the scattering rates, as well as temperature, are presented in Fig. 10 (the solid lines). Here, as we mentioned above, we use a simple model composed of the vacuum and the p-GaAs substrate. The complex dielectric function $\epsilon(q, \omega)$ is given by Eq. (5.6). The same experimental data shown in Fig. 9 (spectra A, B and C) are also shown in Fig 10 (the dotted lines). The best fit with the experimental data is obtained by setting values of the scattering rate Γ at 64, 76, and 86 meV for the spectra taken at 80 K, 200 K, and 300 K, respectively. Thus, the calculations suggest that this temperature effect, i.e. the broadening and shift of the hole-plasmon loss peak, might be due to the temperature dependence of the scattering rate.

Scattering rate

Figure 11 shows the scattering rate Γ_s deduced from the HREELS spectra as a function of temperature (the solid squares), and values of Γ_B calculated from the bulk resistivity of the same sample (the solid circles), using the Drude scattering rate:

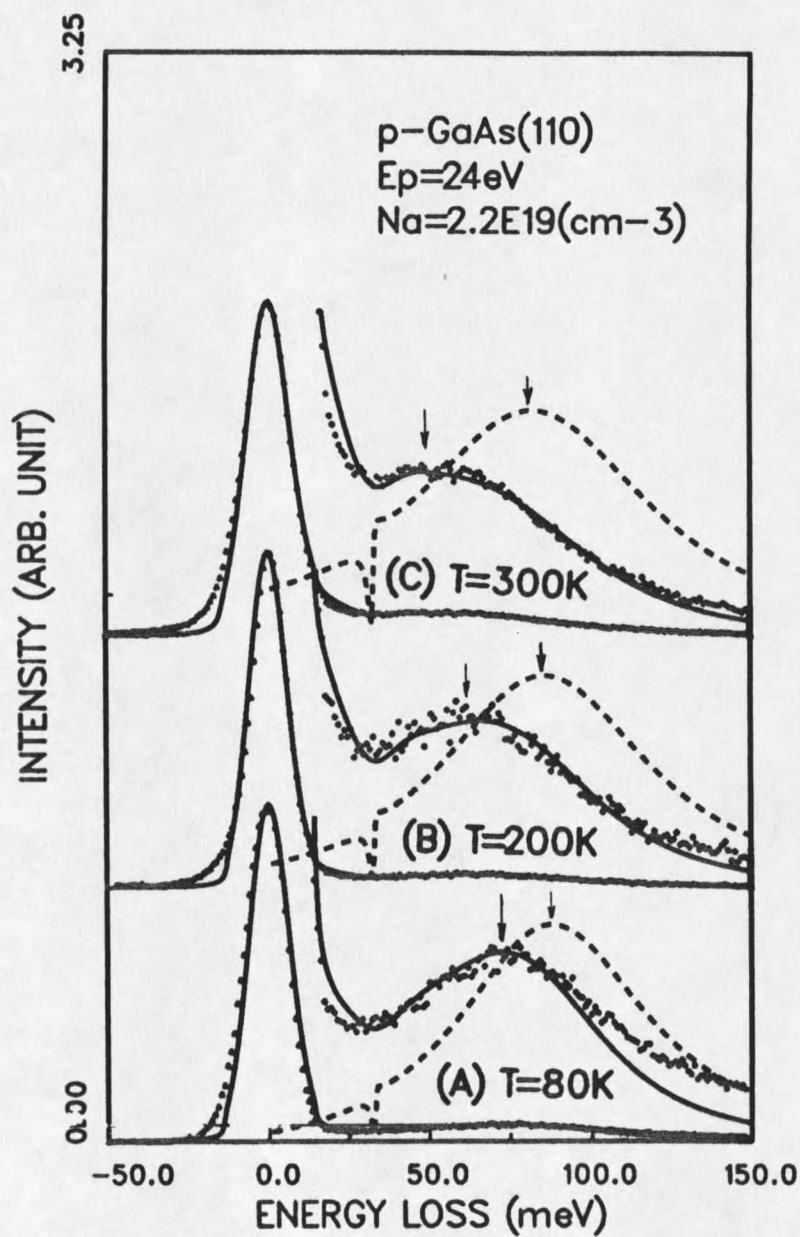


Fig. 10 The solid lines: the calculated EEL spectra with (A) 64 meV, (B) 74 meV, (C) 86 meV. The dashed lines: the products of the loss function and Bose-Einstein factors

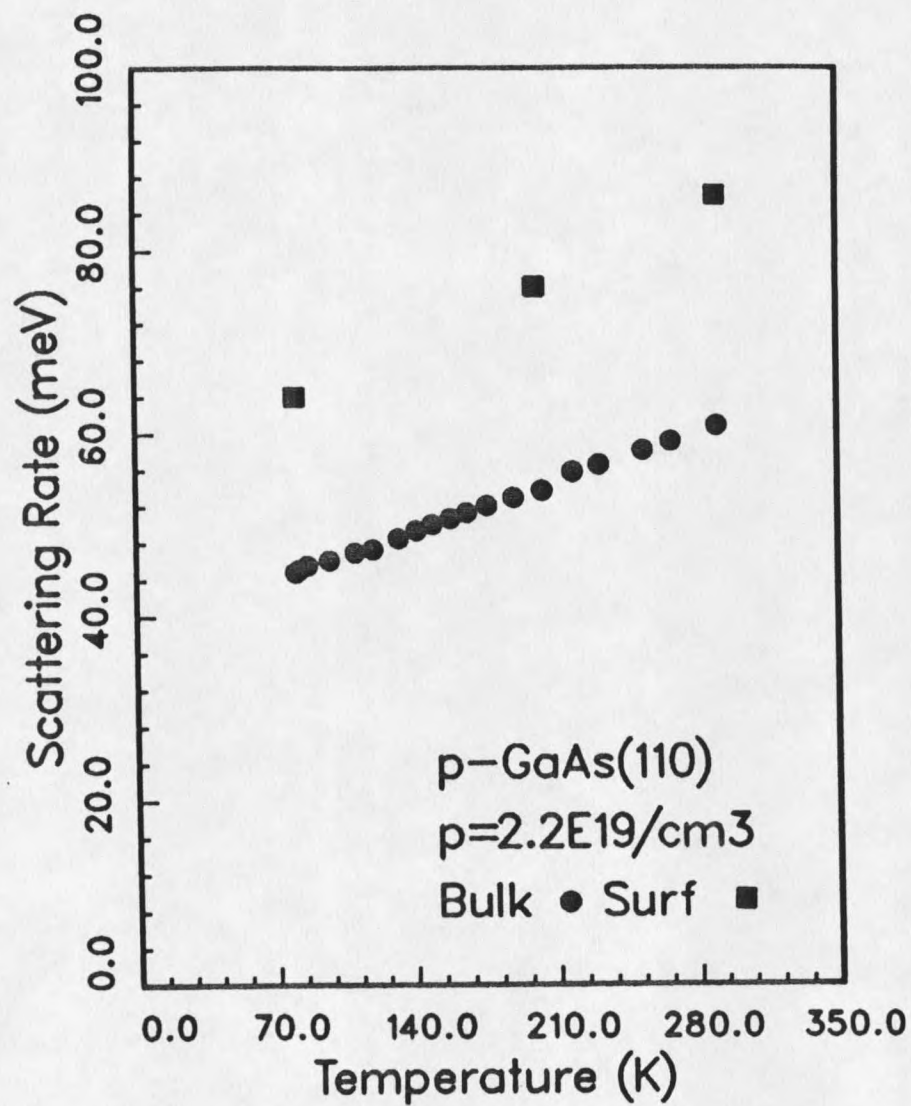


Fig. 11 The bulk (solid circles) and surface (solid squares) scattering rates of holes.

$$\Gamma_B(T) = \frac{e}{m_\sigma^* \mu_H(T)} = \frac{e^2 n_H \rho_B(T)}{m_\sigma^*} \quad (5.9)$$

where m_σ^* is the hole conductivity effective mass, n_H the total hole density, and $\rho_B(T)$ the bulk resistivity. The bulk resistivity ρ_B is measured by a conventional method using a Wheatstone bridge. Complete agreement is achieved between the ratio of $\Gamma_s(300 \text{ K})/\Gamma_s(80 \text{ K})$ (≈ 1.34) from fitting the HREELS data and that of $\Gamma_B(300 \text{ K})/\Gamma_B(80 \text{ K})$ (≈ 1.34) from the bulk conductivity measurement, although there are definite deviations between the absolute values of Γ_s and Γ_B at certain temperatures. Thus, our results strongly suggest that the broadening and shift observed for p-GaAs spectra are due to the temperature dependence of the surface scattering rate. On the other hand, if we convert our surface scattering rate Γ_s to the surface resistivity ρ_s according Eq. (5.9), the surface resistivity of the clean surface is still close to the bulk one while the two resistivities have the same order of magnitude, there is a deviation $\sim 50\%$.

Other effects for kinematical factor

In the previous studies for n-GaAs,¹⁰ the position of the plasmon loss peak is considered as a monitor of the electron density, in the sense that variation of the density profile can lead to a shift of the loss-peak position. Here we present evidence that the variation of the scattering rate can also lead to the peak shift, through the

kinematical factor (see the calculated spectra of Fig. 10 (the solid curves)). In Chapter IV, we showed that the loss probability function $P_{\text{loss}}(\omega)$ can be constructed as the product of the kinematical factor and the loss function. In addition, we note that Eq. (4.16) is valid at zero temperature, while at a finite temperature there is an extra factor $n(\omega, T) + 1$,⁴ where $n(\omega, T)$ is the Bose-Einstein factor. Therefore we have

$$P_{\text{loss}}(\omega) = \frac{2e^2 v_{\perp}^2}{\pi \hbar^2} (n(\omega, T) + 1) \int_0^{q_{\text{max}}} dq_{\parallel} K(q_{\parallel}, \omega) P(q_{\parallel}, \omega), \quad (5.10)$$

where $q_{\text{max}} = k_F \Delta\theta$, $P(q_{\parallel}, \omega)$ is the loss function and $K(q_{\parallel}, \omega)$ is the kinematical factor. To show the significance of the kinematical factor, we calculate $P_{\text{loss}}(\omega)$ in the absence of the kinematical factor $K(q_{\parallel}, \omega)$, and plot in Fig. 10 (the dashed curves). Clearly, we can see that in the absence of the kinematical factor, the 80 meV hole plasmon peak, with increasing temperature, shifts by a few meV because of the Bose-Einstein factor. The peak's energy position is mainly determined by the hole density, while its width, due to the temperature effect of the scattering rate Γ , increases significantly. Therefore, we conclude that the observed temperature-dependent features in the loss spectra, mentioned in the beginning of this section, are due to the temperature dependence of the hole scattering process, in conjunction with the kinematical factor.

On the basis of the above discussion we can now explain why such a temperature effect is difficult to observe on the spectra of n-type heavily doped samples. In a typical n-GaAs system, the electron mobility is much higher than the

hole mobility, i.e., the scattering rate of electrons Γ_e (<10 meV) is much smaller than that of holes. If Γ_e is smaller than the instrumental resolution, as is often true, the observed peak width is determined by the instrumental resolution, rather than by Γ_e . Thus, the temperature dependence of Γ can not be resolved by monitoring the peak width. On the other hand, if we consider the peak energy position of the peak, as we discussed in the last section (see Eq. 5.8), a typical value of Γ is considerably smaller than the surface plasmon energy (e.g., with $\Gamma \sim$ of 10 meV and ω_{sp} of 86 meV), and the plasmon peak shift is too small to be readily observed.

Interface Hole Plasmon

In the last two sections, we focused on the surface hole plasmon and its temperature dependence. The results of these studies reveal that the hole plasmon has properties similar to the electron plasmon, except for the significantly higher scattering rate. The contribution of co-existing light-hole and heavy-hole plasmons in p-GaAs to the dielectric function, is equivalent to that of a single hole plasmon whose energy is given by Eq. 10. In this section, we discuss the interface hole plasmon mode, for the case where a depletion layer is present at the surface.

Interface plasmon mode

A collective excitation in which the plasmon propagates along the boundary

between two media of different dielectric response is called an interface plasmon. In the interface limit, where the depletion layer is treated as a semi-infinite medium, the energy of this interface plasmon mode can generally be given by Eq. (1.1) or Eq. (5.2). For the intermediate case where the thickness of the depletion layer is finite, the interface plasmon energy is bounded by the surface plasmon energy and that for the interface limit. This result can be applied to the present case: if a depletion layer is formed on the surface, the energy of the hole-plasmon interface mode ranges from 63 eV (the interface limit) to 86 eV (the surface limit).

We are able to form a depletion layer on p-GaAs(110) by exposing the surface to atomic hydrogen.¹⁰ Fig. 12 shows three HREELS spectra (the dotted curves): the spectrum (A) taken at room temperature for the clean surface, and the spectra (B) and (C) taken at room temperature and 80 K respectively, after exposure to 100 L of dissociated hydrogen on the clean surface at room temperature. We find that, in spectrum (C), two loss features are visible: one at ~ 35 meV due to the Fuchs-Kliwer phonon, the other at ~ 60 meV which may be attributed to the interface hole plasmon. In spectrum (B), the plasmon-loss peak feature is broadened out, and evolves into a strong shoulder, which, most likely, is due to the large increase of the scattering rate with temperature. The clean surface spectrum (A) is used for comparison.

We use a two-layer model (vacuum/depletion layer/bulk substrate), to examine the hole plasmon response in this H-exposed p-GaAs(110) system. All parameters used here are those obtained from the clean-surface calculation discussed in the first

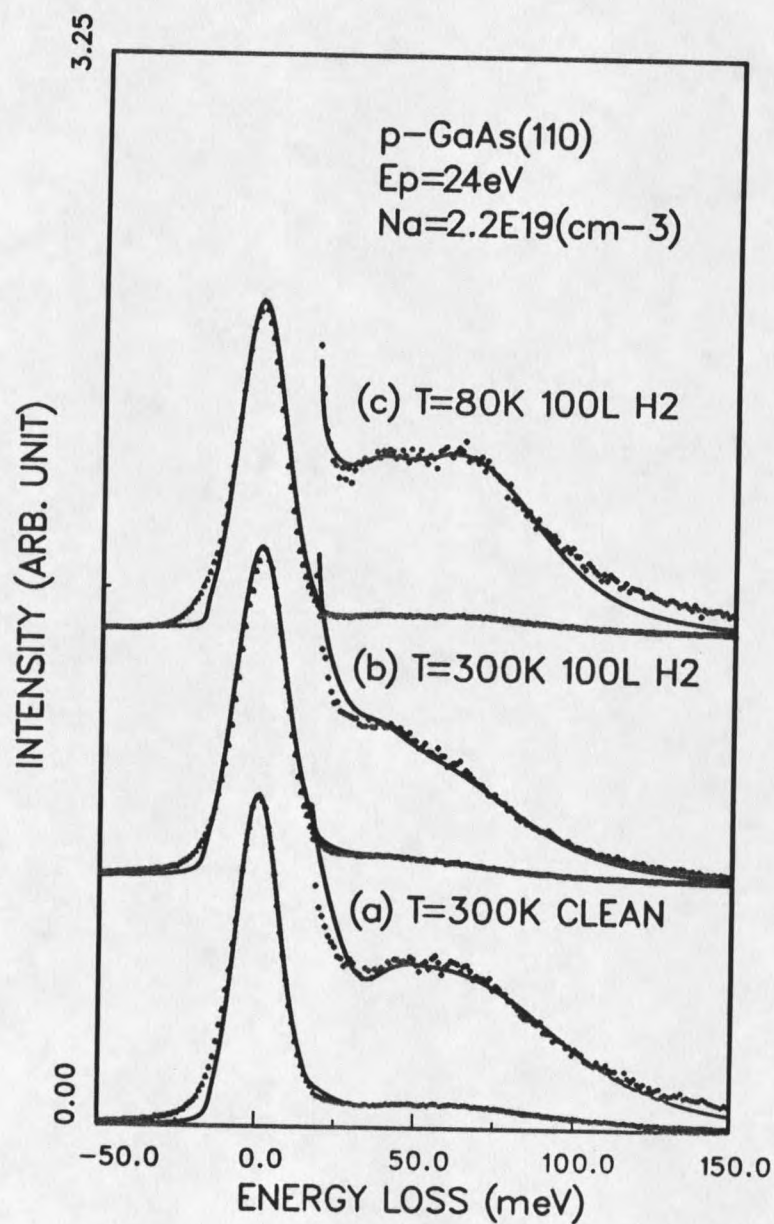


Fig. 12 The HREELS spectra before and after hydrogen exposure (dots). The solid line is the calculated spectra for a two-layer model.

section except for the thickness of the depletion layer. The calculated spectra for three cases are shown in Fig.12 by solid curves. By fitting the spectrum (C), the depletion layer thickness is found to be 45 Å which corresponds to a band bending of 0.31 eV. With this value in hand, we then calculate the theoretical spectrum (B) without changing any parameters except that Γ is increased from 64 to 86 meV because of the temperature dependence we discussed above. One can see that the calculated data fit the experiment quite well, confirming that the loss feature broadening in spectrum (B) is due to the scattering process. In addition, the fitting of spectrum (C) reveals that the observed feature at ~60 meV is due to the interface plasmon mode.

Observation of "dead layer" in p-GaAs

In previous n-type GaAs studies, the presence of a "dead layer", i.e., a layer near the surface where the carrier density is zero, has been suggested by many authors.^{10,13} This dead layer is due to the vanishing of the wave function of the free carriers at the surface; unlike a true depletion layer, it has no net charge.

We are able to explore the possible dead layer by observing the primary-energy dependence of the loss features such as the phonon and plasmon peaks. This is because with higher primary energy, the probe depth of HREELS is larger, so that the probing electron can penetrate deeper into the surface to "see" the interface plasmon excitation under the dead layer. With lower primary energy, however, the probing beam can only "see" the excitation near the surface, i.e., the Fuchs-Kliwer

phonon in the dead layer. Figure 13 shows the HREELS spectra with several primary energies at room temperature. The spectra were taken just after the sample was cleaved, i.e., the surface is assumed to be clean. From these spectra, one can see that the loss feature due to the hole plasmon has a strong dependence on the primary energy. For spectra taken at higher primary energies (e.g., 24 eV), the loss feature for the hole plasmon is quite intense; while for the 1 eV spectrum, it becomes hardly visible. Contrary to the hole-plasmon loss, the loss feature due to the Fuchs-Kliwer phonon at ~ 35 meV is visible in the 1 eV spectrum. Thus, these data imply the existence of the dead layer. The HREELS data fitting indicates the thickness of the dead layer is about (10-20) Å, which is close to the value for an n-type dead layer at high doping level (10-20 Å for 4×10^{18} /cm³).

To conclude this chapter, we attempt to interpret the p-GaAs data of Ref. 7 based on our study. In Ref. 7, the authors found that for a heavily doped p-GaAs(100) surface ($n_H = 1.0 \times 10^{19}$ cm⁻³), the HREELS spectrum has two features that differ from those of the n-type sample: (1) no well-defined plasmon peak is observed, (2) the spectral FWHM is large and the relative intensity of the tail of inelastic loss is high. We simulate this case by using the two-layer model mentioned before, and assume a depletion layer has been formed as a consequence of the cleaning process.⁹⁴ The calculated spectrum is shown in Fig. 14. The parameters used in our simulation are 1.0×10^{19} cm⁻³ for n_H , 100 Å for the depletion layer thickness, corresponding to a band bending of 0.7 eV, and 75 meV for the scattering rate Γ . The calculated result shows

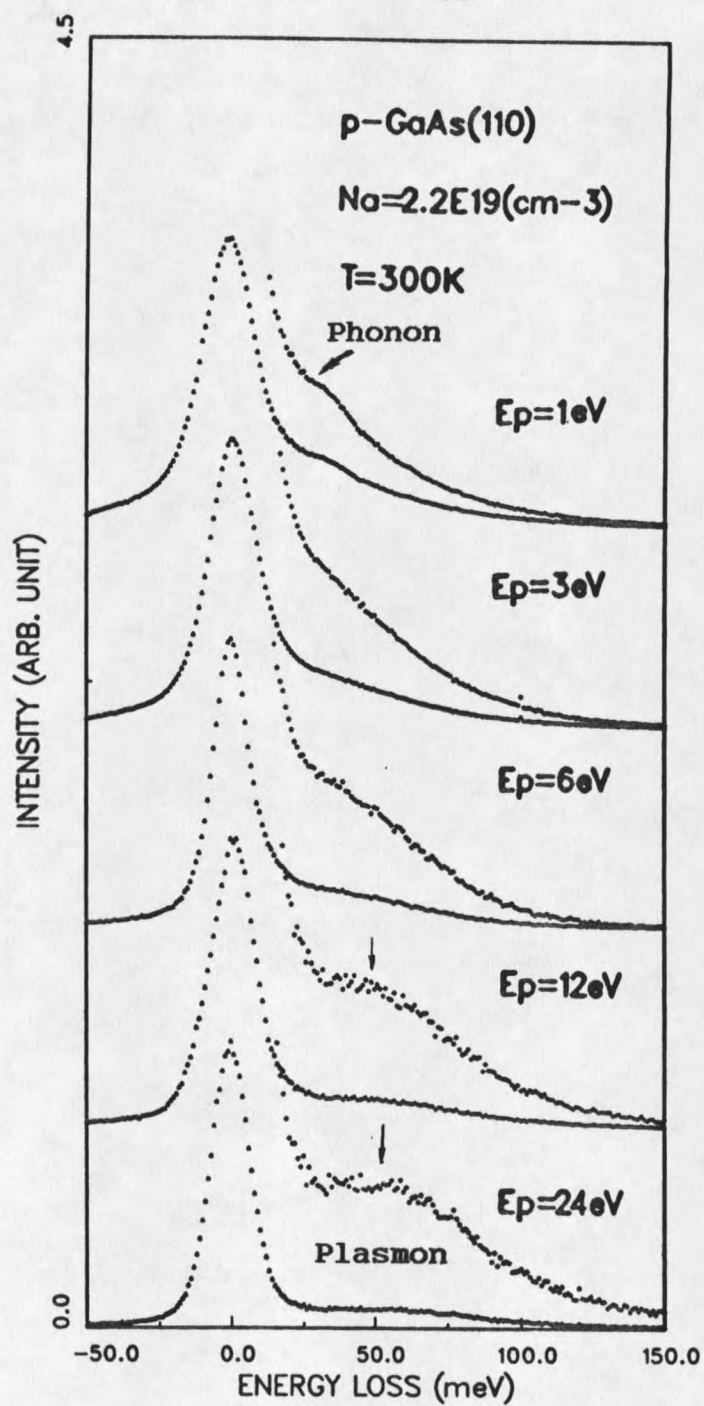


Fig. 13 HREELS spectra with different primary energies at measured at room temperature.

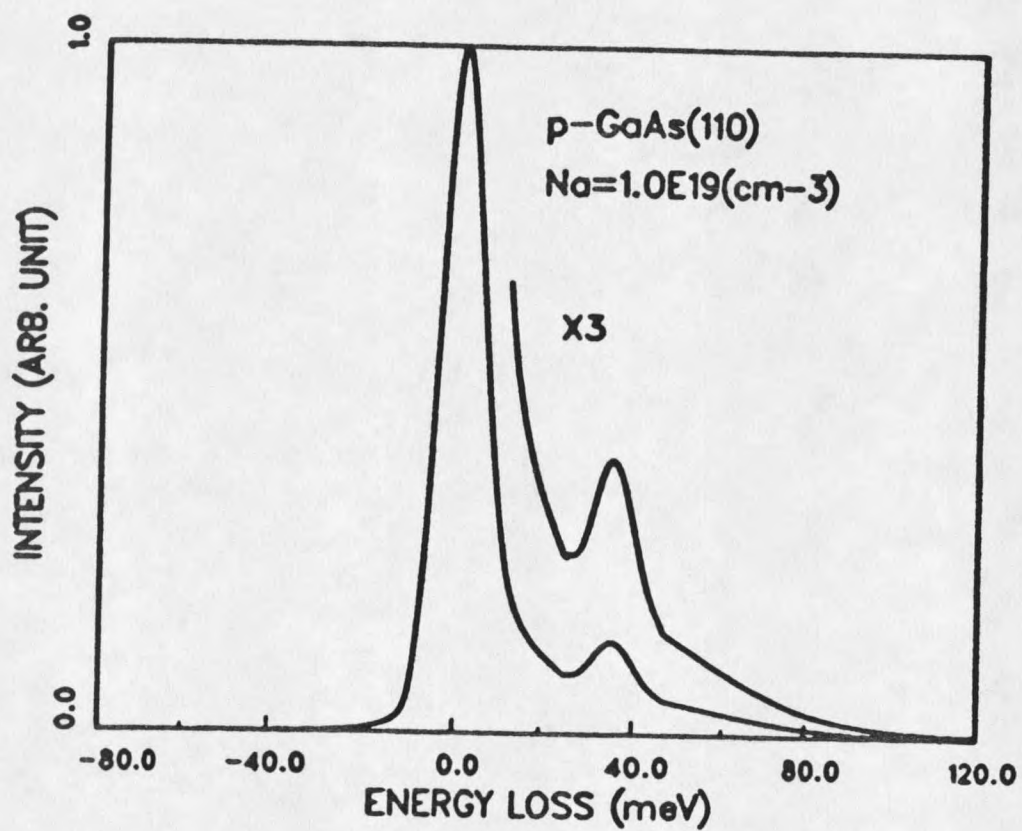


Fig. 14 The calculated HREELS spectrum for the case of Ref. 7 with a two-layer model ($\Gamma=76$ meV, $n_H=1\times 10^{19}$ /cm³, $d_{\text{dep}}=100$ Å)

that (1) good agreement is obtained between our calculation and the experimental data of Ref 7; (2) indeed, as the authors mentioned, no well-defined surface plasmon loss feature is evident in the spectrum; the only well-defined loss feature is the optical-phonon loss. Further calculation shows that both the phonon and plasmon peak appear in the calculated HREELS spectrum if Γ is changed from 75 meV to 10 meV. The absence of the plasmon peak in the case of Ref. 7 is due to the large scattering rate Γ that strongly damps out the plasmon oscillation, and leads to a broad background.

CHAPTER VI

COLLECTIVE EXCITATIONS IN OVERLAYER SYSTEMS

In this chapter we study collective excitations in overlayer systems, such as Bi/GaAs(110), ZnSe/GaAs(110), and ZnSe/Bi/GaAs(110) systems. We begin with a brief description of the interface structure for Bi/GaAs(110) and ZnSe/GaAs(110), since to study the collective excitations at heterostructure interfaces experimentally, one must have a model interface system, i.e., an ordered and nondisruptive interface. Next we present the HREELS observation for the two-dimensional overlayer plasmon in Bi/GaAs(110), and the observation for the surface and interface optical phonons in ZnSe/GaAs(110), and compare them with the theoretical calculations. Finally, we present the results for ZnSe/Bi/GaAs(110) and discuss the ZnSe overlayer phonon excitations in the monolayer regime.

Interface Structure

Most III-V semiconductor interfaces are reactive and disruptive. The Bi/GaAs(110) and ZnSe/GaAs(110) interfaces are among the few interfaces which can

be considered as model systems for epitaxial growth.

For the case of the Bi/GaAs(110) interface, recent studies indicate that Bi exhibits a Stranski-Krastanov (SK) or modified SK growth mode on GaAs(110).³³⁻⁴⁰ The first Bi monolayer grown on GaAs(110) at 300 K forms an ordered (1×1) overlayer consisting of Bi zigzag chains along the [1T0] direction accompanied by an ordered array of vacancies to relieve strain in the ordered Bi terraces. The geometric model for this overlayer is the bulk extended model.^{74,75} Additional deposition of Bi results in island growth atop the initial monolayer (ML). Epitaxial interface development shows no interdiffusion between substrate and overlayer or disruption of the semiconductor surface. In addition, photoemission data indicate that the first overlayer is semiconducting, and at larger coverages, the overlayer becomes (semi)metallic.

ZnSe has a lattice constant very close to that of GaAs. The lattice mismatch $f = (a_{\text{GaAs}} - a_{\text{ZnSe}}) / a_{\text{GaAs}}$ (a_i the corresponding lattice constants) is only 0.265%. Previous LEED and AES studies show that, by congruent evaporation on GaAs(110), the epitaxially grown ZnSe films are nearly stoichiometric and form an abrupt interface with the substrate.⁵⁴ Our LEED and XPS studies agree with the previous results: a sharp 1×1 LEED pattern is found in the low coverage regime (<4 ML). Even at a coverage of 18 ML of ZnSe, where the substrate signals are not observed by XPS, a 1×1 LEED pattern could still be observed although the background was higher, which suggests some order for the ZnSe overlayers.⁴³

Bi/GaAs(110) System

High-resolution electron-energy-loss spectroscopy (HREELS) has previously been used to study the Ag/n-GaAs(110)³⁰ and Sb/n-GaAs(110)³² interfaces. Dubois *et al* studied Ag/n-GaAs(110) in the coverage regime of a few monolayers (0-10 ML). The results show that, for Ag/n-GaAs(110), when the Ag overlayer was deposited on the substrate at 170 K, a disordered uniform film was formed with a highly metallic character; a distinct background wing due to the two-dimensional electron plasmon in the Ag overlayer was seen to develop and increase out to coverages of 2.5 Å where the substrate Fuchs-Kliever phonon peak was no longer visible in the loss spectra. If deposited at room temperature or warmed to room temperature after being deposited at 170 K, the Ag overlayer formed a metallic island. The spectra thus show significant reduction of the wing intensity (the background), and the distinct loss feature due to the Fuchs-Kliever (FK) phonon in the underlayered GaAs substrate can be observed.

The Sb/n-GaAs(110) system has been studied by Annovi *et al.*³³ The results show that in this system no loss features due to the two-dimensional overlayer electron plasmon are observed for coverages below 15 ML, which indicates the Sb overlayer is semiconducting in that region. For the lightly doped GaAs sample (1×10^{17} /cm³), the HREELS spectra are dominated by the FK phonon peak (1-30 ML).

In this section, we present our HREELS results for the Bi/GaAs(110) system, and analyze them with the classical dielectric model. We also show that in the few

monolayer regime, the Bi overlayer on GaAs(110) is semimetallic, unlike either Sb (semiconducting) or Ag (metallic), and it undergoes a transition from a semiconductor to a semimetal at a coverage of 1.5 ML.

Experimental results

HREELS data of the Bi/GaAs(110) interface for the clean GaAs surface and several Bi coverages from 0 to 10 ML, are shown in Fig. 15. The clean cleaved spectrum (the bottom curve) shows two peaks which are due to a Fuchs-Kliwer phonon excitation at 35 eV and an electron plasmon excitation at 60 meV for n-GaAs(110) ($n \approx 2.3 \times 10^{18} \text{ cm}^{-3}$). Bi films deposited on GaAs change the surface Fermi level position, forming an electron depletion layer. Thus, the strength of the electron plasmon mode in the GaAs substrate is diminished with the formation of the depletion layer, and the Fuchs-Kliwer phonon peak appears to be relatively strong, as shown in the 0.1 ML spectrum. When the Bi coverage increases above 1 ML, the sharp phonon peak starts to broaden, and the background develops. At 10 ML, the phonon feature is invisible.

In addition, by carefully examining the differences among these spectra, as shown in Fig. 16, one observes that the phonon peak position for the 4 ML spectrum shifts to 2 meV higher than that for 0.1 ML, and the background for 4 ML is distinctly higher than that for 0.1 ML (feature A).

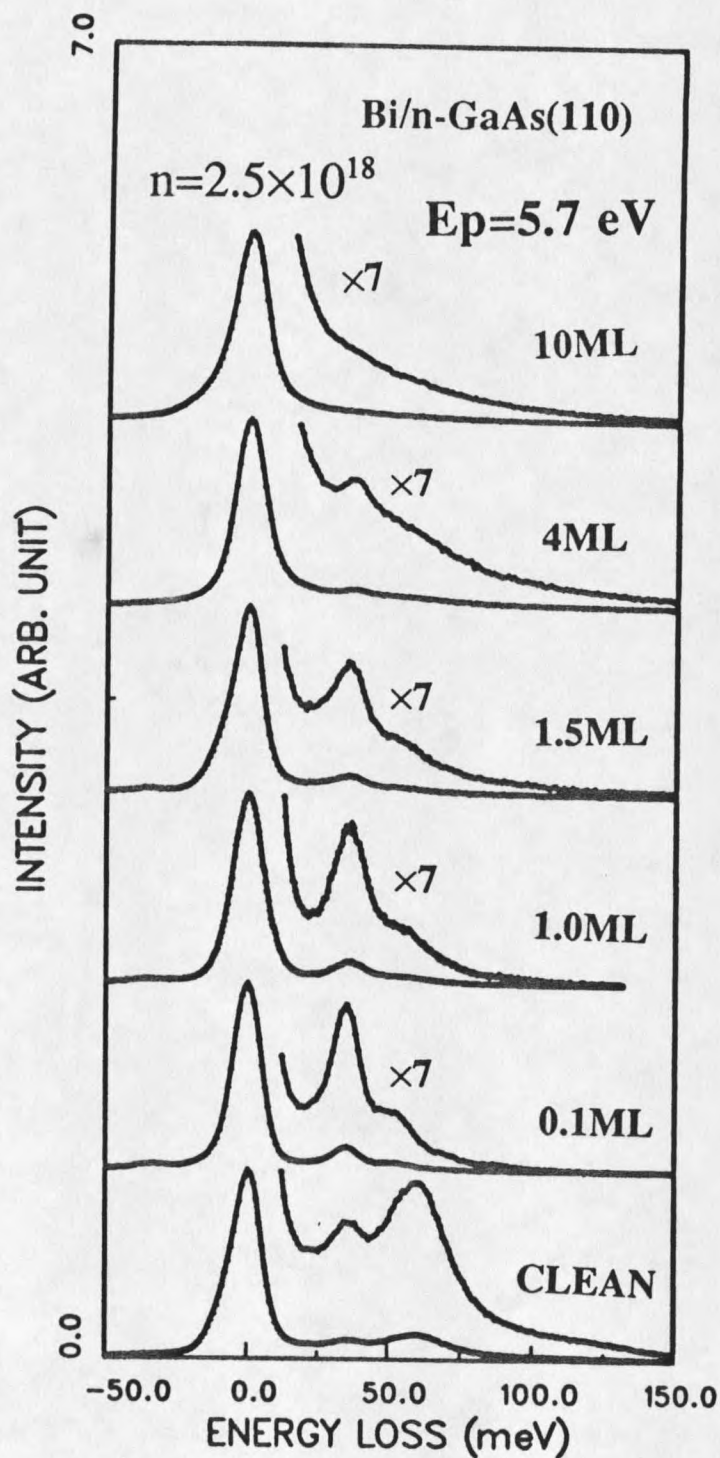


Fig. 15 HREELS spectra of the Bi/n-GaAs(110) interface for the clean GaAs(110) surface and several Bi coverages from 0 to 10 ML.

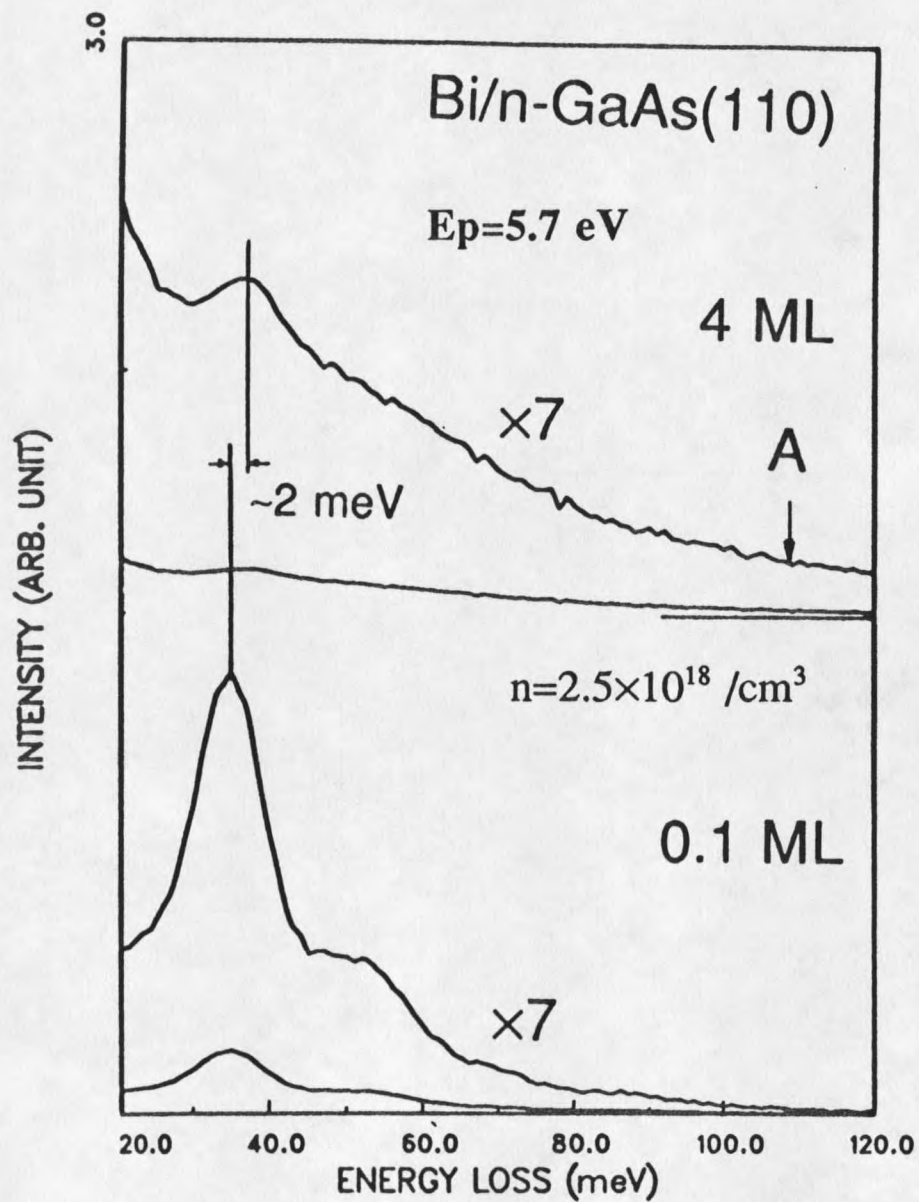


Fig. 16 Two HREELS spectra of Bi/n-GaAs(110) with coverages of 0.1 ML and 4 ML in a smaller energy scale.

Discussions and modelling

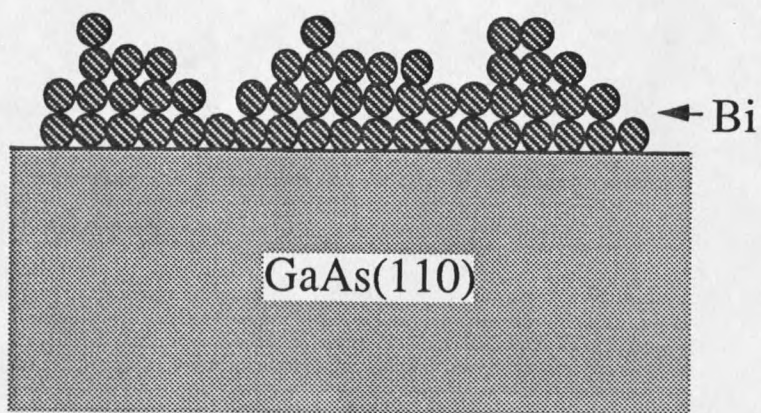
For discussion of the experimental data in Fig. 15, a three-layer model composed of the Bi overlayer, the GaAs depletion layer, and the GaAs substrate, is used to describe the Bi/GaAs interface system. Figure 17 shows the schematic picture for the Bi/GaAs(110) interface morphology and our model for the HREELS calculation. We note that after the first Bi monolayer completely covers the substrate, Bi clusters form atop the layer. However, for simplicity, we still treat this layer as a uniform dielectric layer of thickness d . In addition, since the electron density of the bulk Bi is relatively high compared to a typical semiconductor, the screening effect may be strong,⁹⁵ and so we use the Fermi-Thomas model to describe the dielectric function for the the Bi layer

$$\epsilon_{Bi}(q, \omega) = \epsilon_{\infty}^{Bi} - \frac{\omega_{pBi}^2}{\omega(\omega + i\Gamma_{Bi} - 0.6v_F q^2)} \quad (6.1)$$

where ϵ_i^{Bi} is the background dielectric constant, v_F the Fermi velocity, and ω_{pBi} the Bi plasmon frequency, which is given by $\omega_{pBi}^2 = \frac{4\pi e^2 n_{Bi}}{m_e^*}$, where n_{Bi} is the electron density, and m_e^* the electron effective mass. We neglect the hole-plasmon contribution in the Bi valence band, since, generally, the effective mass of holes is significantly larger than that of electrons.⁸⁰

In this three-layer model, both phonon and plasmon excitations are included in the substrate, but only the phonon excitation is considered in the depletion layer.

Bi/GaAs(110) interface



HREELS Three layers model:

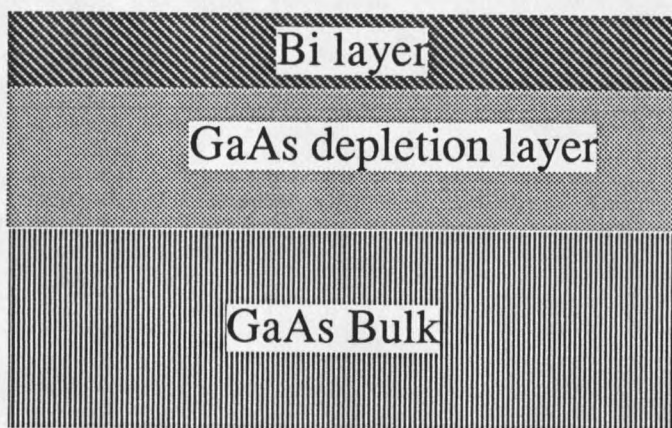


Fig. 17 The schematic for the Bi/GaAs(110) interface morphology, and the model for HREELS calculations.

The depletion-layer thickness in this model is taken as a constant for coverages above 0.1 ML, according to photoemission data, which show that the band bending is almost complete at 0.1 ML of Bi on GaAs(110).³⁶ For the doping density of $2.5 \times 10^{18} \text{ cm}^{-3}$, the depletion layer thickness is $\sim 200 \text{ \AA}$.

The spectra as a function of Bi coverage as computed within our three-layer model are shown in Fig. 18; some of the parameters obtained from fitting the data are listed in Table II. Of these parameters, the electron density is the most interesting one. As seen in Table II, the electron density rapidly increases with the coverage, especially above 1 ML, indicative of a semiconductor-semimetal transition. This is consistent with the photoemission observation that a conversion from semiconducting to semimetallic character occurs when the film thickness increases beyond 1 ML.³⁶ This result also indicates that at high coverages ($>1.5 \text{ ML}$), the Bi layer is semimetallic, not metallic, since the density varies in range of 10^{19} - $10^{20} / \text{cm}^3$, which is a typical region for semimetals (note, in Table II, we show the ratio of $n_{\text{Bi}}/m_{\text{Bi}}^*$, not n_{Bi}).

On the basis of the results in Table II, we make the following conclusion. Below 1 ML of Bi, because the Bi layer is semiconducting, the Fuchs-Kliever phonon mode in the depletion layer is unscreened, so the GaAs FK phonon peak dominates the spectrum. When the coverage is increased to 1.5 ML, the Bi layer is transformed into a semimetallic layer, so that the monotonic loss background develops due to the Bi two-dimensional plasmon. This 2D plasmon mode is described by a dispersion

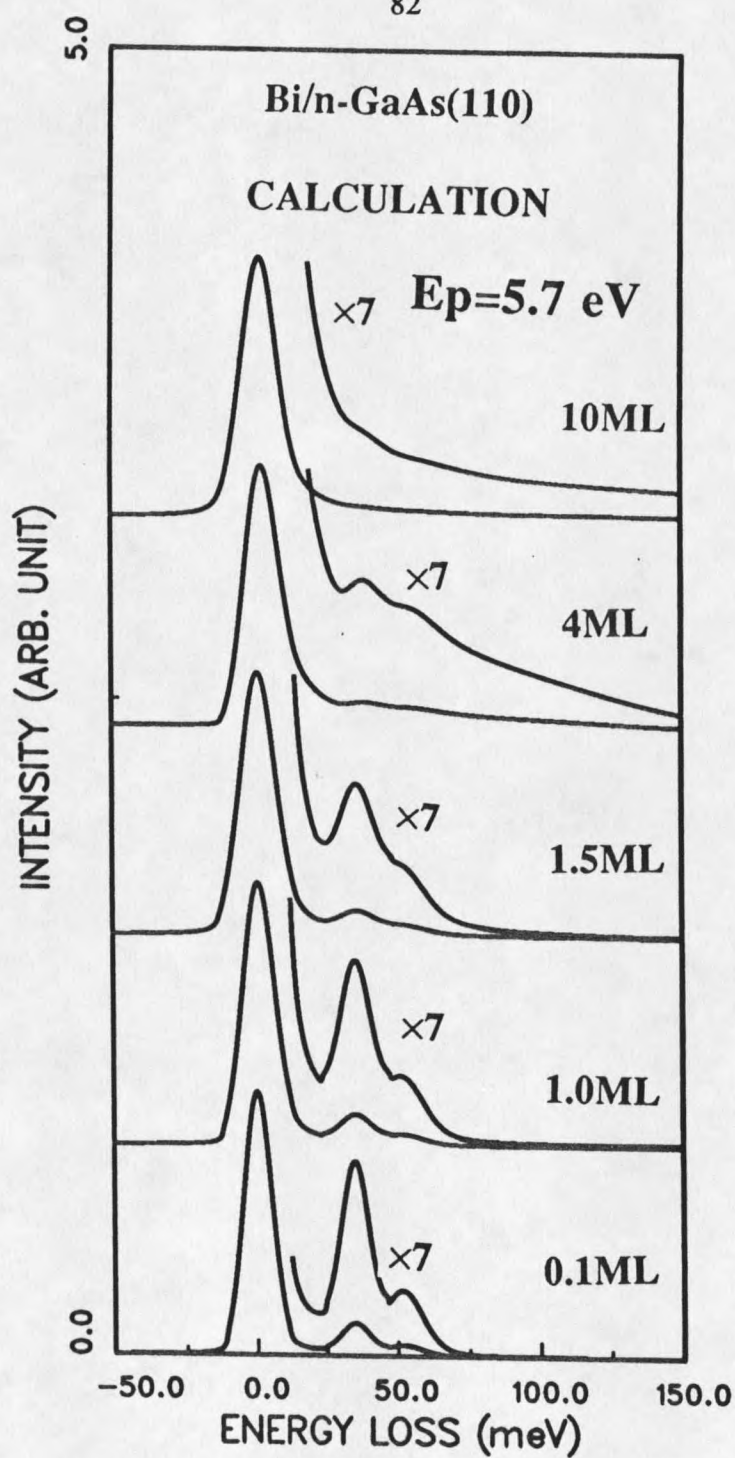


Fig. 18 The calculated HREELS spectra as a function of Bi coverages with a three-layer model. ($n=2.5 \times 10^{18} / \text{cm}^3$, $d_{\text{dep}}=200 \text{ \AA}$).

Table II Parameters of Bi overlayer obtained from fitting of experimental data

coverages (ML)	thickness d_{Bi} (Å)	density $n_{\text{Bi}}/m_{\text{Bi}}^*$ (cm^{-3})	Γ_{Bi} (meV)	$\epsilon_{\infty}^{\text{Bi}}$	m_{Bi}^* ($m_e=1$)
0.1	0.3	-	100	3†	0.18†
1.0	3.0	$<1 \times 10^{20}$	100	3†	0.18†
1.5	4.5	2×10^{20}	100	3†	0.18†
4.0	12.0	1×10^{21}	100	3†	0.18
10.0	30.0	$\sim 2 \times 10^{21}$	100	3†	0.18†

†: the values are not very sensitive during the data fitting.

relation³⁰

$$\omega(q_{\parallel}) = \left(\frac{\omega_p^2 q_{\parallel} d}{1 + \epsilon_{\text{GaAs}}} \right)^{1/2} \quad (6.2)$$

On the other hand, since the phonon mode is screened from the surface, the phonon-peak intensity decreases. With further increases of both the coverage and the electron density, the strength of the 2D plasmon mode increases and reaches its maximum at 4 ML (see Fig. 16), so the loss background now becomes the dominant feature in the spectrum. At 10 ML, the Bi overlayer totally screens the electric field produced by the phonon mode from underlayer GaAs, so that the phonon mode is no longer

detected, leading to a lower background.

The increase of free-electron density in the Bi layer can be attributed to the Bi layer "size effect". This size effect can be explained as follows. As known from basic band theory, the band structure of a crystal can often be described by the nearly-free-electron model, in which the band electrons are treated as being perturbed weakly by the periodic potential of the ion cores. Thus, the energy levels near the center of the Brillouin zone can be approximately described by $E = \frac{\hbar^2}{2m^*}(k_x^2 + k_y^2 + k_z^2)$. Here, the allowed wave vectors k_x , k_y , and k_z are distributed continuously from zero to π/α (α the lattice constant), since the minimum interval in k-space is on the order of $1/L$ (10^{-9} of π/α), where L is the crystal size. However, when the size of the crystal is reduced, for instance, in the z dimension, from L_z to d , the energy levels now become $E = \frac{\hbar^2}{2m}((k_x^2 + k_y^2) + (\frac{\pi n}{d})^2)$. Thus, we can see that the original continuous band may split into several subbands. Now, if some of the subbands are totally filled, the electrons in these bands are no longer free electrons because of the band gaps, so that the total density of the free electrons decreases. Then if the Fermi level of the system lies in the band gap between the subbands, the system exhibits either semiconducting or insulating behavior. The band gap can be estimated as $E_{gap} = \frac{\hbar^2}{2m}(\frac{\pi}{d})^2$, namely a few eV when d is $\sim \text{\AA}$. Note that the gap decreases rapidly with d . Let us now consider the Bi case. For bulk Bi, the conduction band minimum (CBM) overlaps the valence band maximum (VBM) at the Fermi level. The thick Bi film corresponds to this case. When the thickness of the Bi film decreases, band splitting occurs, so that

the CBM and VBM shift away from the Fermi level, in opposite directions. As a result, the overlap vanishes, and a gap between these two bands is formed. Therefore, the thin film becomes semiconducting. In fact, recent inverse photoemission³⁷ and STM³⁹ results for Bi/GaAs(11) have shown that the band gap (0.7 eV) appears in the submonolayer region, and vanishes when the coverage increases beyond 1-2 ML.

It should be noted that in a high-electron-density overlayer system, two plasmon modes exist for each choice of $q_{\parallel}$ (given by Eq. (4.11)). In the limit $q_{\parallel}d \ll 1$, the first of these is the so-called two-dimensional mode, described by Eq. (6.2) which gives vanishing energy as the wave vector ($q_{\parallel}$) $\rightarrow 0$. For the second mode, the energy is very close to the bulk plasmon energy; this mode sometimes is called the three-dimensional mode. We attempted to observe this three-dimensional mode in the relevant energy region. However, no indication for a well defined loss feature was found. The related spectrum was calculated, and we found that the ratio of the calculated intensity for this plasmon loss peak to that of the elastic peak is $\sim 1/5000$. Thus, since the counting rate of the elastic peak is typically on the order of $\sim 5 \times 10^3$ /sec after Bi deposition (10^5 /sec for the clean surface), it appears that the loss feature for this mode is undetectable.

During the data fitting, we found that for low coverages (0.1-1.5 ML), the spectra calculated using both the Fermi-Thomas model shown in Eq. (6.1) and the Drude model (which ignores dispersion) in the Bi dielectric function, have a good agreement with the data. However, for higher coverages, especially for 4 ML, only

the Fermi-Thomas model gives a good fit, which suggests that the electron-electron interaction in the Bi layer might take place in the high coverage region, because of the rapid increase of the free-electron density. Thus, since the dispersion term is a function not only of the free electron density, but also of the electron effective mass, from the data fitting using the Fermi-Thomas model, we are able to obtain the value of the electron effective mass, which is $0.18 m_e$. This value is consistent with the result in the literature that the effective masses in the pentavalent semimetals are generally substantially smaller than the free-electron mass.⁹⁵

We note that, in their EELS calculations for Ag/GaAs(110) at coverages of ~ 1 - $2.5 \text{ \AA}$, Dubois *et al* observed an asymmetric phonon line shape due to the interaction between the substrate phonon and the two-dimensional plasmon, and concluded that the experimental data provide no evidence for this theoretical prediction. In our calculations we find a similar situation for Bi/GaAs(110). In the presence of the conducting Bi layer, the phonon line exhibits an asymmetric shape, even a highly asymmetric dip in the very broadened background at high coverages. However, we find that by taking into account the instrumental broadening, the asymmetric phonon line shape turns into a nearly symmetric peak standing on the inelastic background, but its peak position shifts toward higher energy. For a coverage of 4 ML, the calculated peak position is at $\sim 37.5 \text{ meV}$. This result is consistent with our experimental data in Fig. 16. Therefore, our Bi/GaAs data appear to provide evidence for the substrate phonon-two dimensional overlayer plasmon coupling.

ZnSe/GaAs(110) System

High-resolution electron-energy-loss spectroscopy (HREELS) has previously been used as a surface- and interface-sensitive technique to probe the interface phonon in GaAs/Al_{0.3}Ga_{0.7}As superlattices and the CaF₂/Si(111) epitaxial insulator-semiconductor structure, both grown by MBE.^{87,88} The results of those investigations showed that in the former case⁸⁷ the experimental results are well described by the classical dielectric theory. In the latter case, the classical approach failed for ultrathin overlayers, probably because of either the quantum limit⁸⁸ or the strain between the overlayer and substrate (atomic forces). In this section, we present HREELS results for the ZnSe/GaAs(110) system, and show that the ZnSe/GaAs(110) interface is similar to the GaAs/Al_{0.3}Ga_{0.7}As system, in which the classical dielectric theory gives a successful description of the ultrathin overlayer cases.

Experimental Results

HREELS spectra of the ZnSe/n-GaAs(110) interface for the clean GaAs surface and two ZnSe coverages are shown in Fig. 19. Curve A (the clean cleaved GaAs surface) shows two peaks: a Fuchs-Kliwer phonon excitation at 35 meV and a plasmon excitation at 60 meV. The ZnSe films deposited on GaAs change the surface Fermi position, forming a depletion layer. The spectrum for 3 ML is shown by curve B in Fig. 19. The strength of the plasmon mode is decreased with the

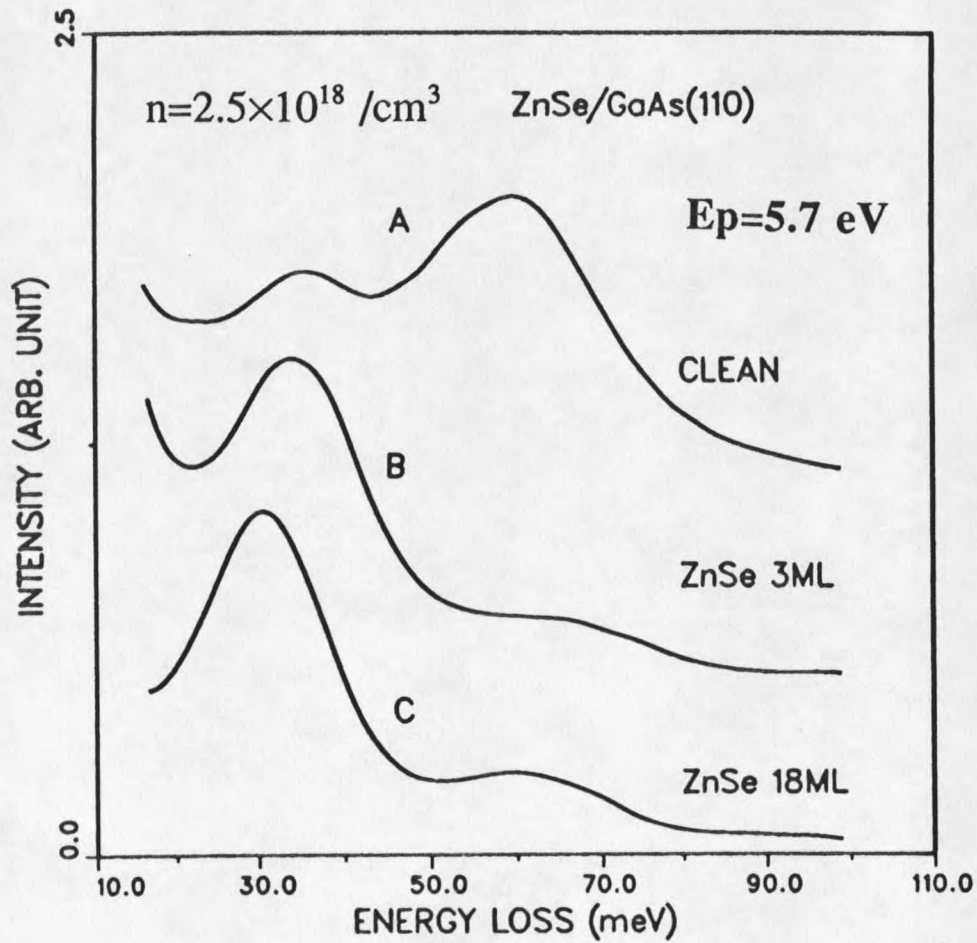


Fig. 19 (A) HREELS spectrum of a clean n-GaAs(110) surface ($2.5 \times 10^{18} / \text{cm}^3$). (B) and (C) are spectra after deposition of ZnSe of 3 and 18 ML, respectively.

formation of the depletion layer. The phonon peak appears to shift to lower energies, because as discussed below, it is a convolution of two separate modes.

A notable feature of curve C is that a peak at 60 meV becomes observable at a coverage of 18 ML, which implies either the plasmon excitation is again observable because of changes in band bending, or some other excitation is occurring, or it is a double loss feature associated with the 30 meV loss. We were able to make an assignment by measuring the dependence on the primary energy. No variation of the plasmon loss energy as a function of primary energy was observed, which means that this peak does not correspond to a plasmon excitation (see the preceding discussion of the interface plasmon in Chapter V). The composition of the surface was checked with XPS, and it was found that only zinc and selenium appeared in the spectra. This excludes the possibility of excitations of Zn- and Se-substrate stretching vibrations. Thus, the results as noted above suggest that this weak peak corresponds to a double loss of the mode at 30 meV. We believe the mode at 30 meV is the ZnSe surface optical phonon since the measured energy of 30 ± 0.5 meV agrees well with a calculation of the surface phonon energy of a ZnSe single crystal from the relation

$$\omega_s = \omega_{TO} \sqrt{\frac{(\epsilon(0)+1)}{(\epsilon(\infty)+1)}} \quad (6.3)$$

yielding 30.12 meV, where $\omega_{TO}=24.85$ meV⁸⁹ is the energy of the bulk transverse optical phonon, $\epsilon(0)=8.1$, and $\epsilon(\infty)=5.2$ are the static and high frequency dielectric

constants respectively.

For further discussion of the "phonon peak", HREELS spectra in the energy loss range of 25-45 meV for several ZnSe coverages from 1 ML to 18 ML are shown in Fig. 20. It is observed that the energy of the peak decreases as a function of ZnSe coverage, and the full width at half maximum (FWHM) is also a function of coverage. The FWHM is greatest at ~4 ML and then decreases as the coverage is increased beyond 4 ML. This dependence of the FWHM on ZnSe coverage will be discussed below.

Discussions and modelling

In order to describe quantitatively the ZnSe/GaAs(110) system, we here present a three-layer model composed of the ZnSe overlayer, the GaAs depletion layer, and the GaAs substrate. This model is similar to the previous Bi/GaAs model except that the Bi overlayer is replaced by the ZnSe overlayer. The depletion layer thickness is taken to be a constant for films thicker than one monolayer, since 90% of the band bending occurs after depositing 0.5 ML of ZnSe on GaAs(110) as is indicated by the high-resolution photoemission data.⁹⁰ The thickness of this depletion layer is about 200 Å since the doping density is $2.5 \times 10^{18} \text{ cm}^{-3}$. In the three layer model, both the substrate phonon and plasmon excitations were included, but only the phonon excitation was considered in the top two layers; i.e. the ZnSe overlayer and GaAs depletion layer.

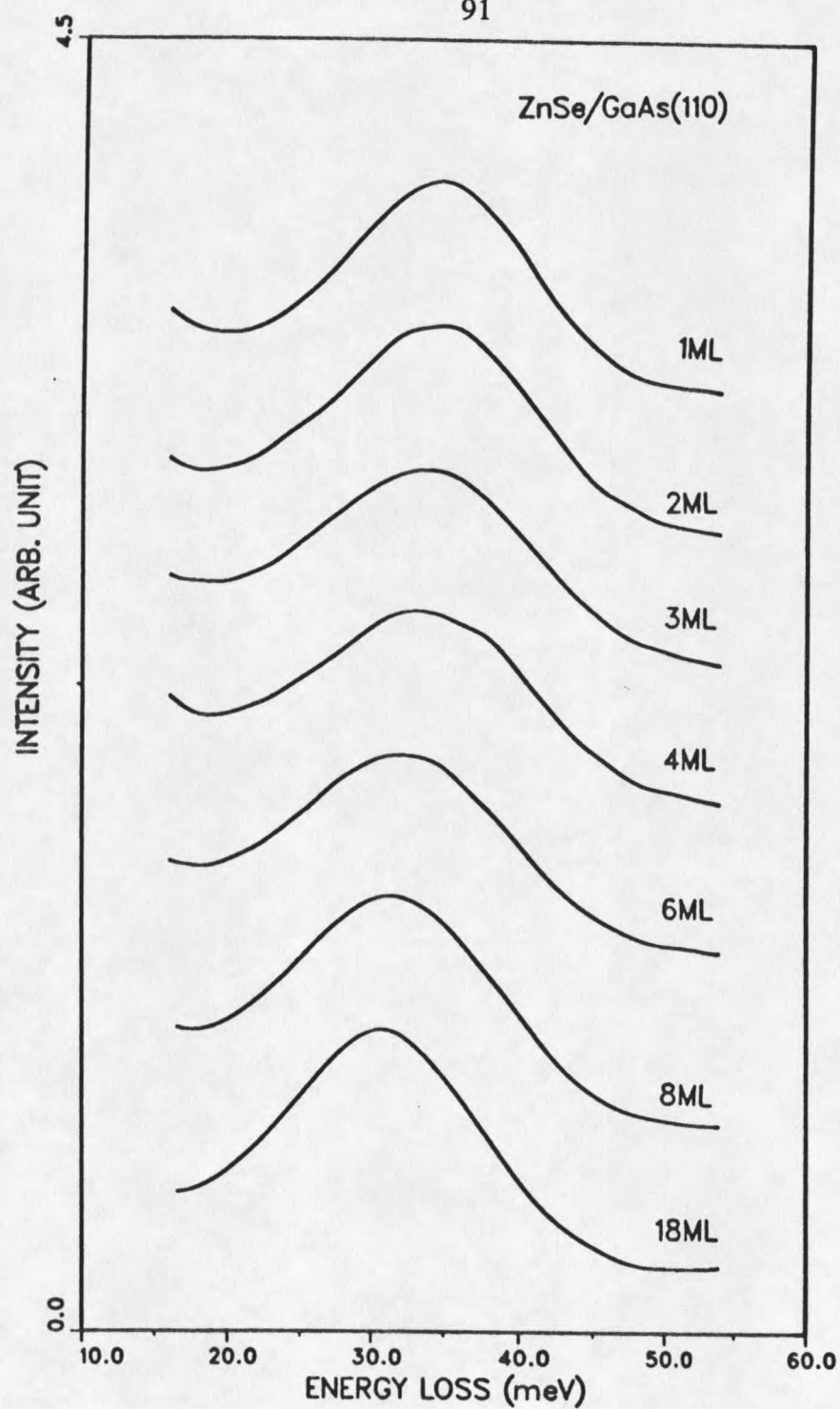


Fig. 20 HREELS spectra of the phonon losses at ~ 30 meV, taken for various ZnSe coverages.

The calculated HREELS spectra as a function of ZnSe coverage using this model are presented in Figure 21. One can see that the ZnSe/GaAs has three Fuchs-Kliwer modes: a ZnSe interface-like mode at ~ 25 meV, a ZnSe surface-like mode at ~ 30 meV, and a GaAs interface-like mode at ~ 35 meV. The ZnSe interface-like mode is weaker in intensity than the latter two modes and it increases with coverage. Thus, the latter two modes produce the phonon peak in the experimental spectra and the ZnSe interface-like mode has essentially no effect. As the ZnSe coverage increases, the loss intensity of the ZnSe surface-like mode increases while the intensity of the GaAs interface-like mode decreases. At a coverage of 4-5 ML, the intensities of these two modes become equal to each other. We also calculate the coverage dependence of these Fuchs-Kliwer phonon modes. The results show that the energies for these modes are slightly dependent on coverage (1 meV for <1000 Å). This suggests that the peak shifting mentioned above and shown in Fig. 20 was not the result of a coverage dependence in energy position for a single mode.

The observed changes in the position of the loss peak maximum can be accounted for by a convolution of two phonon modes. After taking into account instrumental broadening, estimated to be 6 meV, the curves as of Fig. 21 are recalculated and presented in Fig. 22. One can see that the ZnSe interface-like mode is buried in the background, and the other two peaks merge into a single peak with an energy and width dependent on the individual intensities of the two modes. Clearly, at a coverage of 4-5 ML, where the ZnSe surface-like and GaAs interface-like

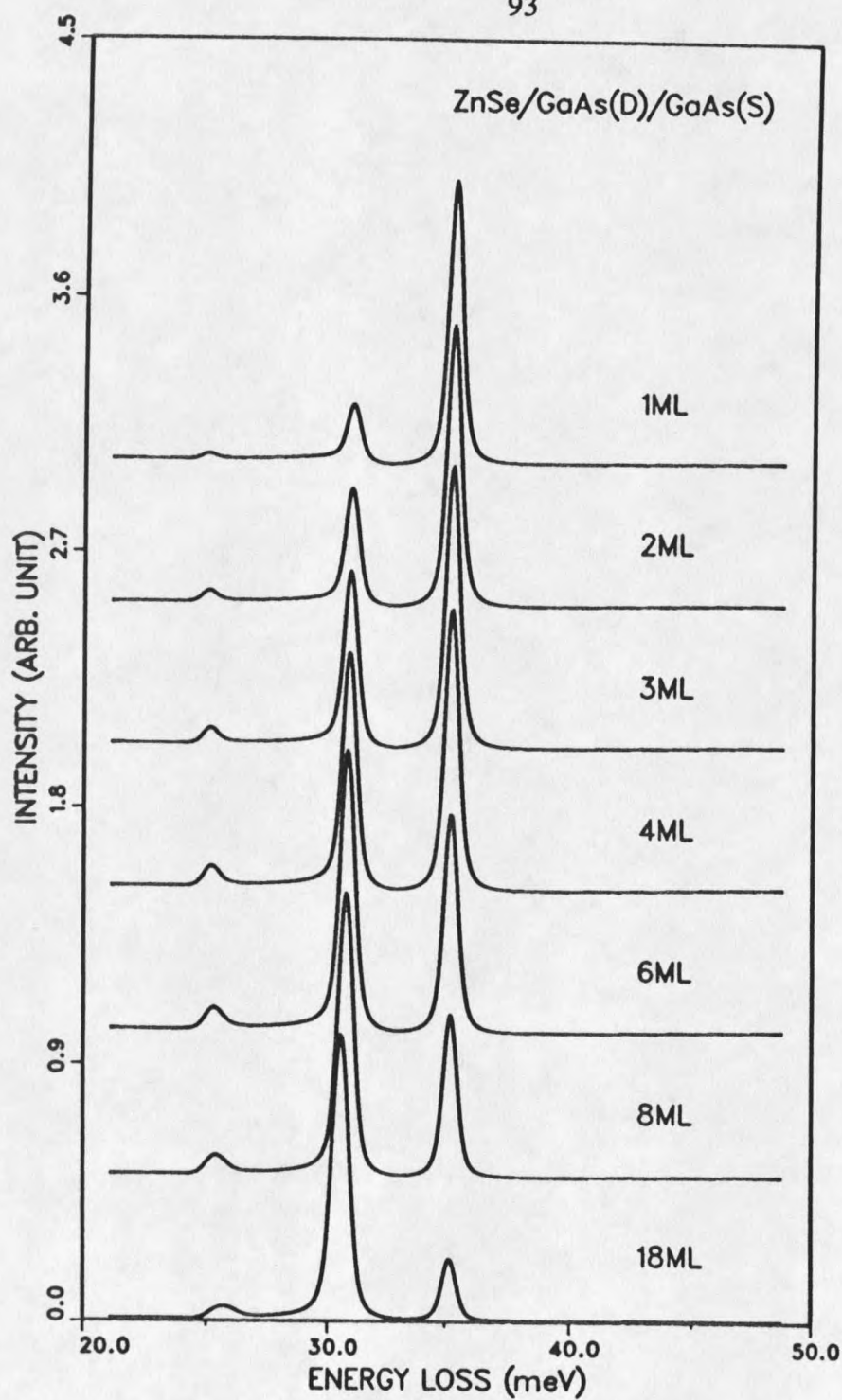


Fig. 21 Calculated HREELS spectra for several ZnSe coverages. A three-layer model is employed, i.e., ZnSe-GaAs(depletion layer)-GaAs(bulk).

mode are approximately equal, the convoluted peak should be broadest, and this behavior is indeed found in the experimental results in Fig. 20. The shift in energy of the maximum of the composite peak from 35 meV to 30 meV is due to the intensity of the two single modes changing with coverage.

For a further discussion of the peak shift, a plot of the composite peak position versus ZnSe coverage is shown in Fig. 23 for both the experimental and calculated spectra. There is a critical thickness (an inflection point) in this curve where the energy position for the composite peak varies rapidly with coverage. From the calculated results in Fig. 24, the critical thickness is found to correspond to the point where the intensities of the ZnSe surface and GaAs interface modes are equal. Thus, this thickness can be considered as a characteristic thickness of the ZnSe/GaAs(110) system for determining the dominant role between the GaAs interface mode and the ZnSe surface mode for ELS studies. The appearance of the inflection point supports the interpretation that the observed peak is a composite of two individual peaks. This critical thickness is a function of the doping density of the substrate (the corresponding calculations are shown in Fig. 23). The physical insight revealed is as follows. For the lower doping density, as we know, the depletion layer (the space-charge layer) at the GaAs surface is wider because of band bending, and the unscreened phonon of the layer contributes more to the loss signal. Thus, for the ZnSe/GaAs(110) system, the relative weight of the GaAs interface phonon mode decreases with increasing doping density because of the decreasing thickness of the

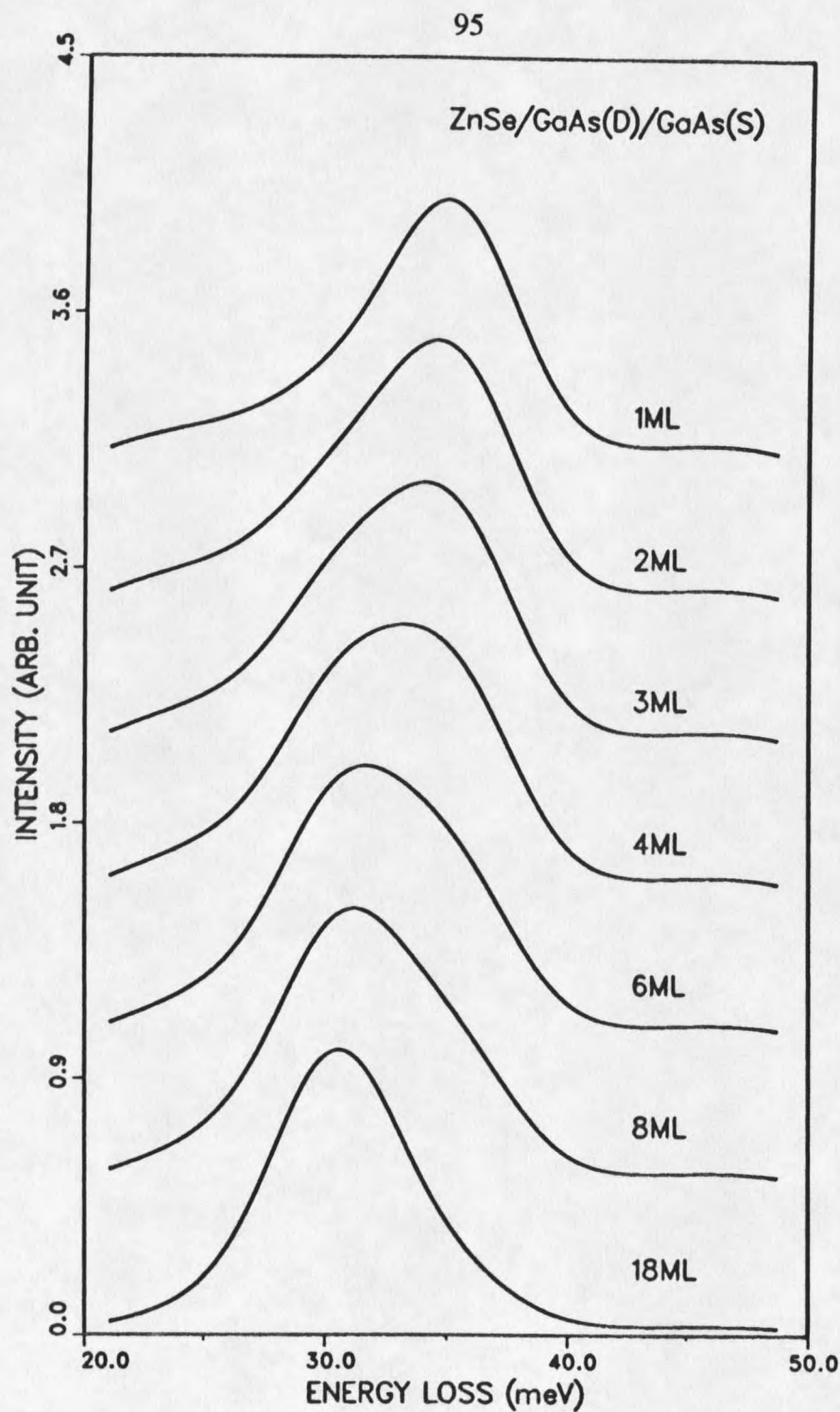


Fig. 22 Calculated HREELS spectra for several ZnSe coverages. An instrumental broadening of 6 meV was used in the calculation.

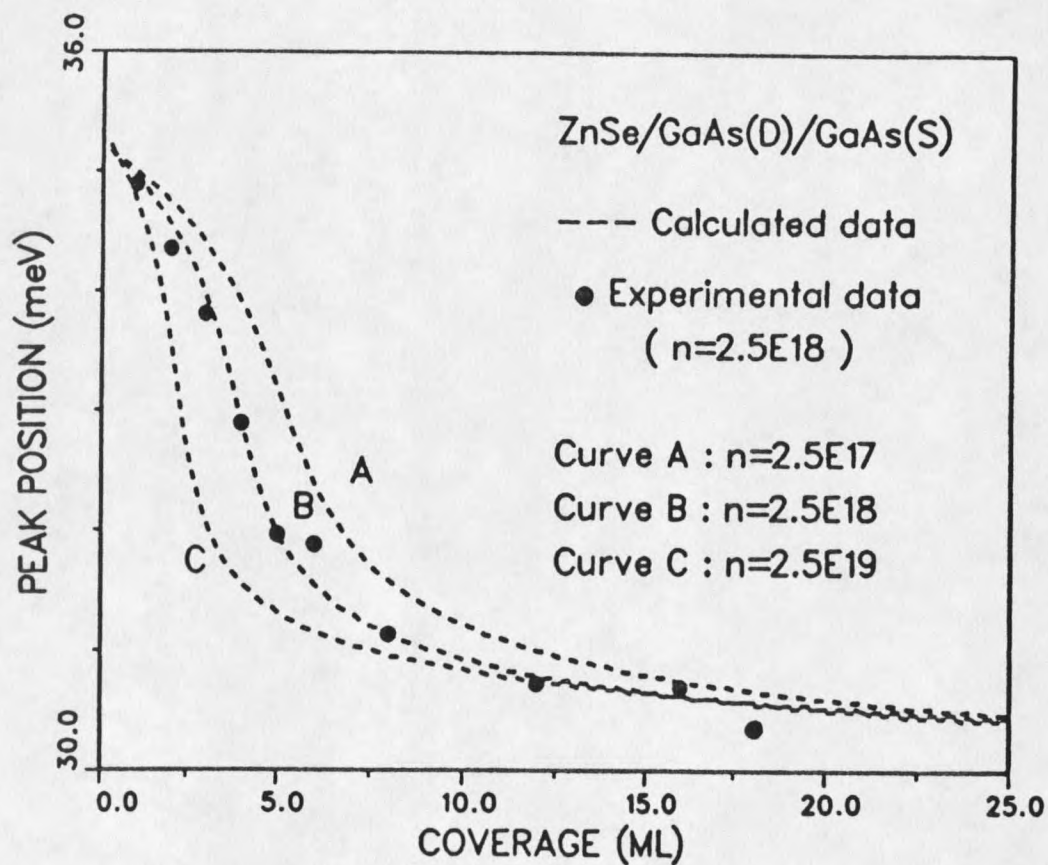


Fig. 23 Composite peak position vs ZnSe coverage: filled circles represent the experimental data ($n=2.5 \times 10^{18}$) and the dashed lines are the calculated curves for several doping densities.

depletion layer. Thus, since the critical thickness corresponds to equal weight of the two modes, the relative weight of the ZnSe surface mode decreases, which leads to the lower ZnSe coverages. Therefore, the critical thickness decreases with doping densities. Consequently, we see that a high doping density is preferred in order to characterize the interface behavior of ultrathin overlayers (2-3 ML) where it is most interesting for studying the two-dimensional properties of an interface, we will come back this point in the section of ZnSe/Bi/GaAs(110).

In addition, we need to mention: 1) for the characteristics of the ZnSe ultrathin film, analysis of the experimental data reveals that the optical phonon excitation exists in an ultrathin ZnSe overlayer even (maybe) in an overlayer of 1-3 ML. This excitation can be described by classical theory, which suggests in the ZnSe/GaAs(110) system no evidence of strain due to lattice mismatch is observed by HREELS as mentioned in Ref. 88. Also no observable evidence of a unique quantum effect in an ultrathin region is found. 2) Good agreement between theory and experiment has been obtained for both the energy position and the shapes of the curve (see Figs. 20, 22, and 23). But we also note that this treatment is based on a classical electrodynamical description, which assumes the layer to be uniformly continuous regardless of the layer thickness. The treatment in this case seems to give good results, even for the monolayer thickness, but a more realistic approach should take into account the discrete and two-dimensional nature of the overlayer.

ZnSe/Bi/GaAs(110) System

It would be very interesting to study collective excitations, such as overlayer optical phonons, and plasma in a model multi-two-dimensional layer system. ZnSe/Bi/GaAs(110) appears to be an ideal candidate for providing such a system, since Bi/GaAs(110) is a model interface system and the system is still ordered after the ZnSe deposition from our LEED observation. In addition, from a physical standpoint, of interest is the study of the initial formation of a collective excitation, such as the ZnSe long wavelength optical phonon mode in a ZnSe overlayer system at coverages in the regime of a submonolayer or one monolayer. As shown in the proceeding section concerning the ZnSe/GaAs study, since the energy difference for the ZnSe surface-like and GaAs interface-like phonon modes is 4 meV, which is smaller than the instrumental resolution $\sim 6-13$ meV, the contribution of these two modes to the loss spectra emerges as a composite peak. To resolve the energy and intensity for the ZnSe surface-like mode, one can deconvolute the observed phonon peak using the theoretical model. However, for the cases where the ZnSe coverages are very small (e.g., <1 ML), the intensity of the ZnSe mode is at the noise level of the GaAs interface phonon mode, so it is difficult to obtain a reliable result for the ZnSe mode. One way to solve the problem is to reduce the intensity of the GaAs interface-like phonon mode by interposing a relatively high conductive Bi layer between the ZnSe layer and GaAs substrate, since the Bi layer can screen the

substrate phonon mode from the surface yielding a relatively enhanced ZnSe mode.

Results and discussions

Figure 24 shows several HREELS spectra of the ZnSe/Bi/GaAs(110) multilayer system. For the 3 ML Bi spectrum (without ZnSe film), one can see that after Bi deposition, the response of the clean surface electron plasmon mode of the GaAs substrate is diminished because of the depletion layer formation, and the surface phonon mode in the depletion layer is also suppressed because of the presence of the conducting Bi overlayer. After depositing 1 ML of ZnSe on the Bi layer, the GaAs FK phonon peak at ~ 37 meV appears to become stronger and the peak position shifts to 34 meV. With further deposition of ZnSe, the peak intensity increases, and it turns into a well defined sharp peak, and the peak position finally shifts to 30 meV which is the energy position of the surface phonon for ZnSe. In addition to the development of the loss feature, a gain feature (a shoulder) appears in the region of 25-35 meV at 11 ML of ZnSe.

For a discussion of the experimental data in Fig. 24, a sandwich model, i.e., a four-layer model which consist of the ZnSe overlayer, the Bi overlayer, the GaAs depletion layer, and the GaAs substrate, is used to describe the ZnSe/Bi/GaAs system. The calculated spectra for several ZnSe coverages are shown in Fig. 25. The calculations are carried out in a straightforward manner, and all the parameters used here are based on the results of the preceding two sections.

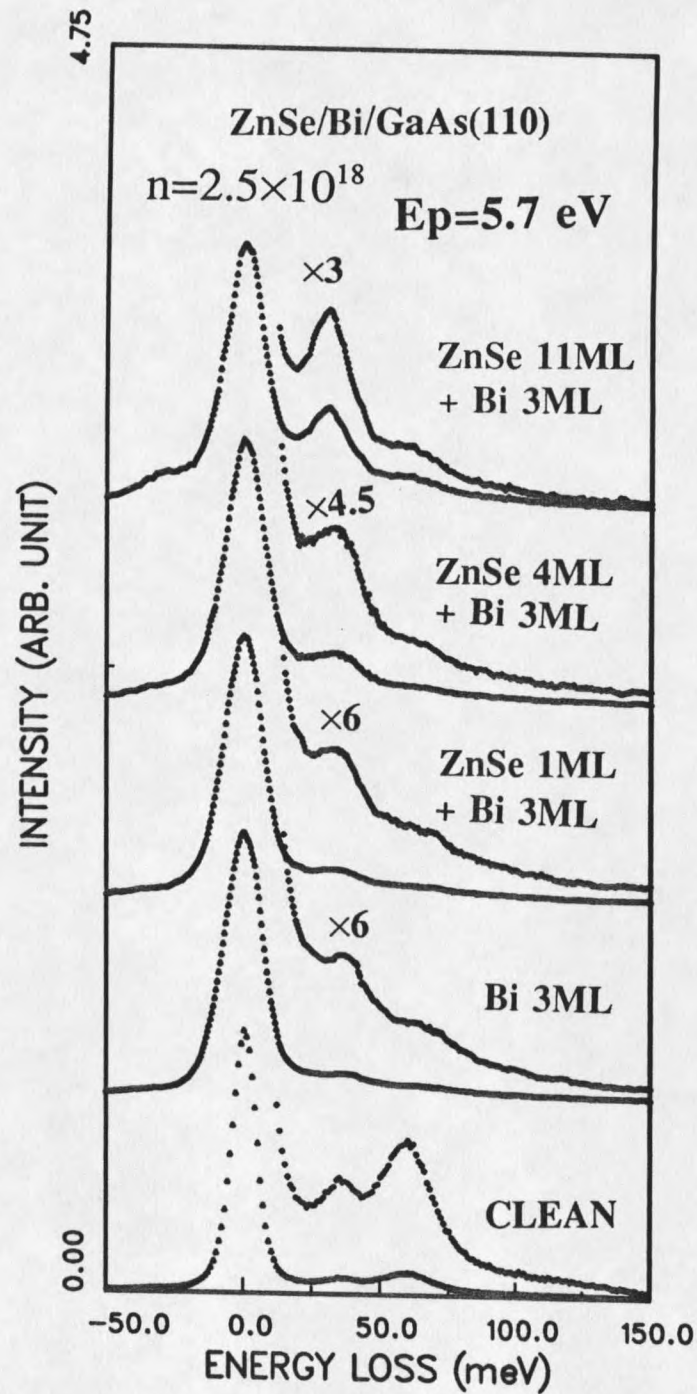


Fig. 24 HREELS spectra of the ZnSe/Bi/n-GaAs(110) sandwich system for the clean surface, 3 ML Bi on GaAs(110), and several ZnSe coverages from 1 to 11 ML.

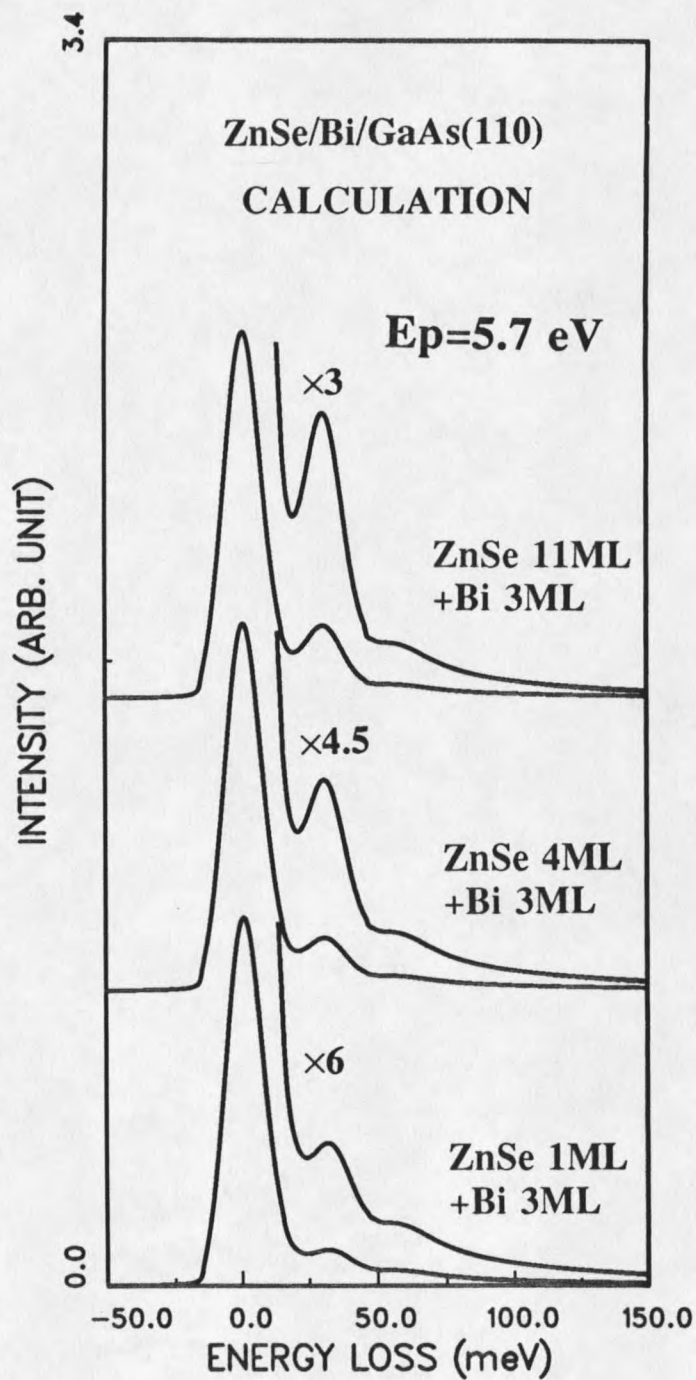


Fig. 25 Calculated HREELS spectra for several ZnSe coverages on Bi/GaAs(110). The model employed is a four-layer model: ZnSe-Bi-GaAs(depletion layer)-GaAs(bulk).

The calculation shows that four excitation modes are visible in the system. They are a ZnSe surface-like mode at 30 meV, a ZnSe interface-like mode at 25 meV, a GaAs interface-like mode, and a 2D Bi plasmon mode (the background). After taking into account instrumentation broadening, as shown in Fig. 25, the ZnSe interface-like mode is buried, and the ZnSe surface-like and GaAs interface-like modes produce a single peak with an energy and a width dependent on the individual intensities of these modes, which is similar to the case of ZnSe/GaAs. This peak stands on the Bi 2D plasmon background.

Compared to the calculated results of the ZnSe/GaAs system, the results of ZnSe/Bi/GaAs show that, as we expected, in the presence of the Bi layer, the intensity of the GaAs interface-like phonon mode is significantly reduced due to the Bi layer shielding, so that the ZnSe surface mode can easily dominate the phonon peak at coverages above 1 ML. At 1 ML, since the peak position is determined by the individual intensities of these modes, an increase of coverages can lead to a significant peak shift from the GaAs mode (~ 37 meV when the Bi layer deposited), to the ZnSe mode (30 meV). Therefore, the peak shift reflects the strength of the ZnSe surface phonon mode.

In Fig. 24, one can see that the phonon peak position is shifted from ~ 37 meV (zero coverage) to 34 meV after depositing 1 ML of ZnSe overlayer on the Bi layer. This distinct peak shift indicates that the long-wavelength ZnSe phonon excitation exists in the very initial stage of the ZnSe thin film (~ 1 ML). In addition, the

observed shift (3 meV) is smaller than the calculated one (5 meV). This may come from the fact that the first ZnSe monolayer does not form a uniform overlayer, but rather ZnSe islands, since the Bi underlayer forms islands on top of the first layer. Thus the effective coverage is probably less than one monolayer.

In addition, it should be mentioned that with coverages up to 11 ML, the loss peak turns into a strong ZnSe surface phonon peak, and the associated gain feature (a shoulder) is observed at around 25-35 meV in the spectrum.

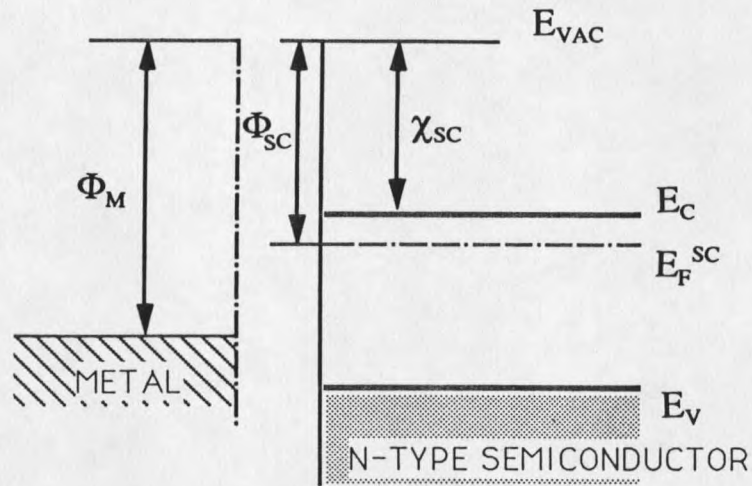
CHAPTER VII

SCHOTTKY BARRIER FORMATION STUDY

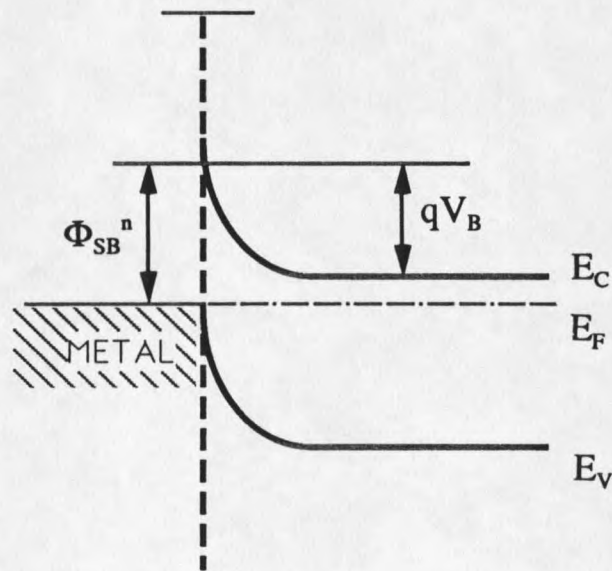
In this chapter, we turn to a new subject, the Schottky barrier formation at metal/III-V compound semiconductor interfaces. We begin with a description of the electrical behavior of metal/semiconductor contacts and a brief review of recent studies for Schottky barrier formation. Next we concentrate on the Bi/InP (110) interface, and discuss the interface structure. We then study the coverage dependence of the band bending and interface electronic structure for Bi/InP(110). We present a unique band bending result for Bi on both n- and p-type InP(110), and propose a charge transfer model based on experimental observations.

Introduction

The band diagram for a metal at an n-type semiconductor surface is shown in Fig. 26, illustrates how a Schottky barrier may form when a metal comes into contact with a semiconductor. After contact, with the two Fermi level E_F^M and E_F^{SC} aligned, electrons flow from the semiconductor to the metal, creating a characteristic depletion



(A) BEFORE CONTACT



(B) AFTER CONTACT

Fig. 26 Schematic of band bending before and after metal-semiconductor contact.

region in the semiconductor. The voltage drop of qV_B across this depletion layer is equal to the contact potential difference between the metal and the interior semiconductor, in the Schottky model.⁴⁴ Thus, the barrier height Φ_{SB} is simply given

$$\Phi_{SB} = \Phi_M - X_{SC} \quad (7.1)$$

where Φ_M is the work function of the metal, X_{SC} the semiconductor electron affinity. However, the Schottky model, described by Eq. (7.1) and illustrated in Fig. 26, unfortunately does not in general describe the behavior of the metal/semiconductor contacts. In many cases, the barrier height for a particular metal/semiconductor interface exhibits only a weak dependence on the work function of the metal. The failure of the Schottky model to describe observed barrier height was addressed by Bardeen,⁴⁵ who proposed that localized surface states can accumulate charge at the interface so as to accommodate the contact potential difference between metal and semiconductor (or pin the Fermi level of semiconductor surface). These localized surface states, usually called interface states, could be intrinsic to the semiconductor surface as described by Tamm with energies in the band gap between conduction and valence bands,⁷³ or intrinsic to the metal/semiconductor contacts as described by the metal-induced gap states model (MIGS),⁴⁷ and might also result from interface imperfections such as irregularities, or foreign atoms in a defect model as proposed by Spicer *et al.*, etc.⁴⁹ The evidence of recent studies using UHV surface sensitive techniques suggest that the Schottky barrier formation is a very complex phenomenon.

It is not universally described by any previously purposed models. Further microscopic behavior occurring during interface preparation, such as interface chemical reaction and diffusion, defect formation, and crystal quality, etc., can affect the charge balance.^{45,52,73}

Therefore, in order to understand the mechanism of the Schottky barrier formation, one needs to minimize these major extrinsic contributions to the barrier formation, so that the resultant metal/semiconductor interfaces exhibit its intrinsic behavior. This approach requires a perfect interface, i.e., an ordered and nondisruptive, and defect-free interface, i.e., precisely interface state-free.

To date only two materials, the recently studied Sb and Bi, are known to form an ordered, nondisruptive monolayer on some III-V semiconductor surfaces, e.g., GaAs(110) and InP(110). Thus, these interfaces provide a good opportunity for investigating various models of Schottky barrier formation.⁵⁶⁻⁶⁹

Strictly speaking, a model interface does not mean an interface that is free of interface states. Recent STM³⁹ and LEED⁴⁰ studies have confirmed that the ordered (1×1) Bi overlayer grown on GaAs(110) at 300 K consists of Bi zigzag chain along the $[1\bar{1}0]$ direction accompanied by an ordered vacancy array to relieve the overlayer strain, induced by the larger size of Bi. The interface states produced by this periodic one-dimensional array of misfit dislocations is $\sim 0.7 \times 10^{14} / \text{cm}^2$, which would be enough to pin the surface Fermi level from a simple calculation of the Bardeen model, even if other surface defects were eliminated completely. (Actually, we find that even

a smaller amount of these interface states, as low as one percent of the surface atomic density ($8 \times 10^{12} / \text{cm}^2$), can significantly change the Schottky barrier height).

In addition, recent STM studies⁶⁴ of Sb/GaAs(110) indicate the interface states can also be created by the irregularities of Sb layer and edges of Sb terraces. These interface states could be eliminated by a thermal annealing process. This is because at high temperature Sb atoms have a large lateral mobility so that the irregularities and islands formed at room temperature (because of the low mobility of Sb atoms on surface) can be smoothed out and turn into a well-ordered Sb monolayer.^{57,68} Recent band bending results appear to confirm annealed Sb/GaAs(110) to be a defect-free (or nearly free) interface, since the surface Fermi position returns to the clean surface case after annealing.⁶¹ However, this annealing process at a high temperature (>500 K) also results in the desorption of the Sb in excess of 1 ML, i.e., only one monolayer of Sb is left on the surface, so the study of the band bending at a higher coverage (>1 ML) is limited.

The Bi/InP interface is better suited to the present study, because InP has a larger lattice constant ($5.869 \text{ \AA}$) than GaAs ($5.654 \text{ \AA}$) so that the unit cell of InP should accommodate the large Bi atom more readily than GaAs, which means no vacancies are induced. In fact, recent dynamical LEED results show the Bi adatoms form a well defined $p(1 \times 1)$ overlayer on InP, and there are no additional structures observed, such as the (6×1) symmetry for Bi/GaAs(110).⁹⁶ In addition, Bi has a higher lateral mobility on surfaces at room temperature,⁵⁷ so the annealing is not necessary

to obtain a nearly defect-free interface, which allows us to study the high coverage dependence of the band bending.

Interface Structure

For a determination of the interface structure of Bi/InP(110), high-resolution core level energy-distribution curves (EDC's) of the In 4d and P 2p levels as well as the Bi 5d levels are used. Figure 27 shows In 4d (left) and P 2p (right) core level EDC's with Bi deposition at 300 K. The spectra are analyzed for multiple components where the composite is compared to the data using a nonlinear, least squares, minimization routine. The two components observed for the clean surface correspond to emission from atoms in the bulk (label 1) and atoms at the relaxed surface (label 2). The relative binding energy of surface component for In 4d is 0.3 eV higher the bulk component, while 0.29 eV lower than the bulk component for P 2p line. Increase of the Bi coverage leads to the loss of the surface component for both core levels. The surface component vanishes completely when the Bi coverage is increased to ~ 1 ML for both cases. In addition, one can see, for both the In 4d and P 2p spectra, the component due to emission from In and P atoms which are bonded to Bi atoms seems not being resolved, which suggest the Bi-In and Bi-P bonding have the same (or nearly same) energy as the bulk extensive bonding. This is consistent with the current results of Miyano *et al.*⁶⁷

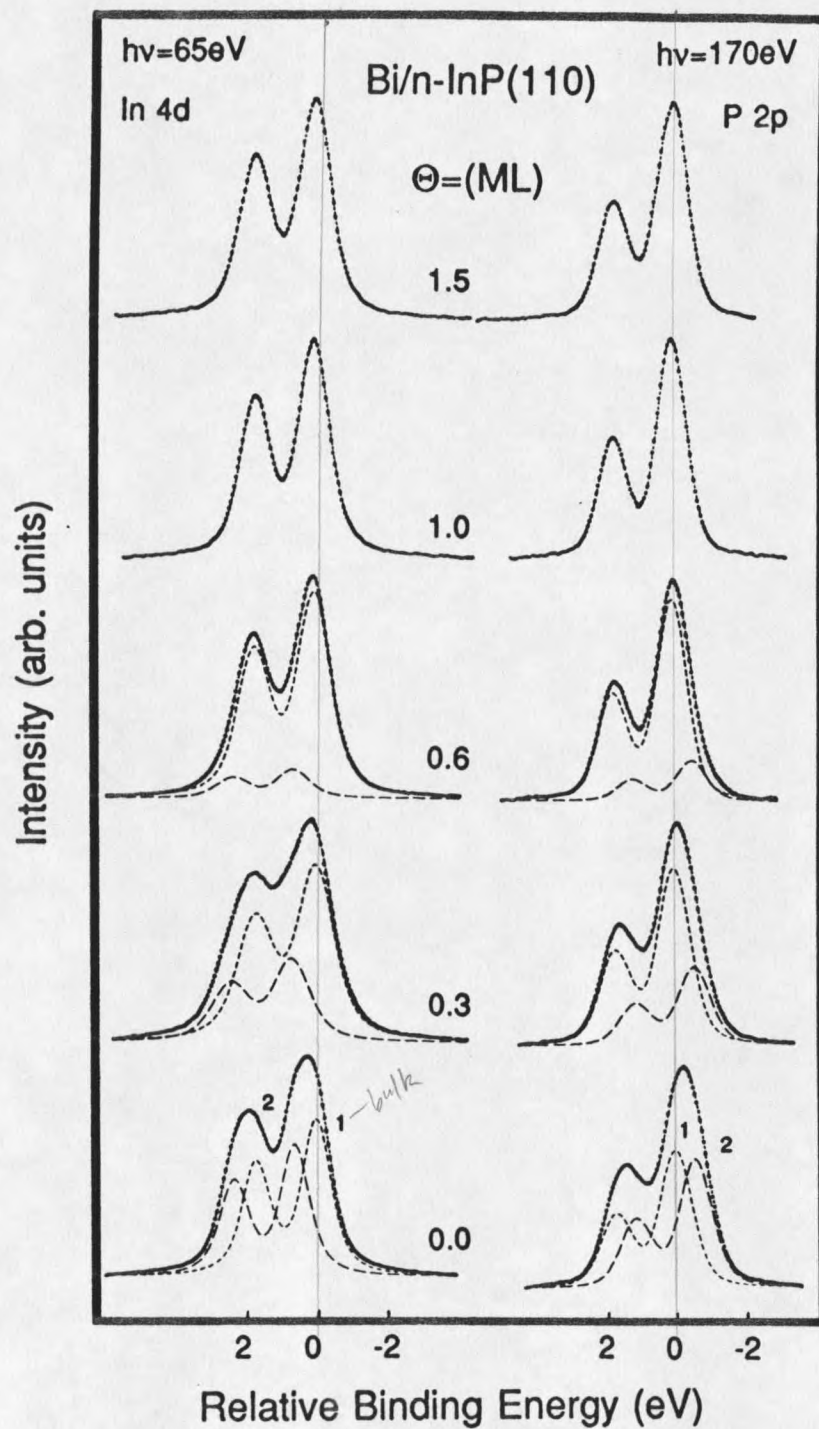


Fig. 27 In 4d (left) and P 2p (right) core level EDC's with Bi deposition at 300 K.

The evidence for Bi-In and Bi-P bonding can be found in the Bi 5d EDC's shown in Fig. 28. For Bi coverages of less than 1 ML, the Bi 5d spectra could be fitted with two components of nearly equal intensity (one at 0 eV and another at 0.42 eV), which could be attributed to Bi sites with neighbors of In atoms and P atoms. Above 1 ML, the third component at -0.28 eV grows, and dominates the spectra above 2.5 ML, and it can be attributed to Bi sites with only Bi neighbors.

Therefore, on the basis of above results and our previous attenuation results for the In 4d and P 2p line,³⁵ we conclude that (1) the Bi/InP(110) interface structure is an ordered and nondisruptive interface; (2) the growth morphology for this interface is the Stranski-Krastanov mode. That is, in the 0-1 ML regime, Bi atoms are bonded to surface In and P atoms forming one ML thick terraces (may be a zigzag chain model as in Sb/GaAs(110)^{13,14}). This is followed by clustering of additional Bi adatoms above 1 ML.

Coverage Dependence of Band Bending

Band bending studies

For most metal-semiconductor interfaces, the surface Fermi level position changes with the development of interfaces. Previous studies for Bi on both n- and p-type GaAs(110), have shown that the band bending increases monotonically with coverage.³⁶ However, we found the band bending for Bi/InP(110) is quite different.

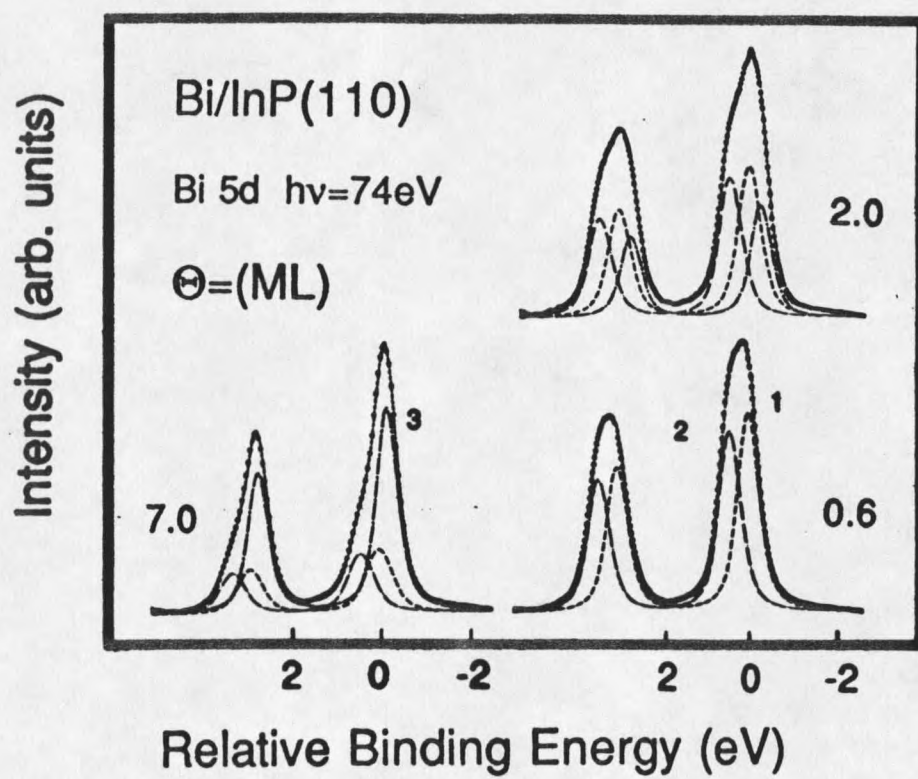


Fig. 28 Bi 5d core level EDC's with Bi deposition.

Figure 29 shows the position of surface Fermi level within the InP band gap as a function of Bi coverage on both n- and p-InP(110) at room temperature. Here, the shifts are monitored by the position of the bulk component of the In 4d line of bulk-sensitive spectra. The experiment was repeated several times making sure that the starting surface was unpinned. For the Bi on n-type InP(110), as the upper curve shows, the clean, freshly-cleaved surface shows flat-bands. The behavior for coverages less than one monolayer may be explained in terms of states at the peripheries of the terraces. A rapid change of the Fermi level position occurs in the region of less than half of one monolayer. This can be reasonably attributed to interface states created by the irregularities of the Bi layer and peripheries of Bi terraces based on the STM observation for Bi/GaAs(110).^{39,64} For the n-InP case, an increase of the Bi coverage up to 1 ML evidently eliminates most of the interface states, and the band bending decreases to the small value of 0.1 eV which perhaps is due to states associated with residual disorder on the surface.⁴⁹ Such interpretation can be further supported by the annealing experiments of Esser *et al*⁶¹ where the band bending due to Sb on n-GaAs(110) and n-InP(110) is found to vanish when the film is annealed at a temperature where the Sb in excess of 1 ML desorbs. For increasing coverage above 1 ML, there is a slow increase in the band bending, which we attribute to the variation of the Bi density of states with coverage. This point is discussed in detail below.

For the p-type InP (the lower curve in Fig. 29) the band bending increases

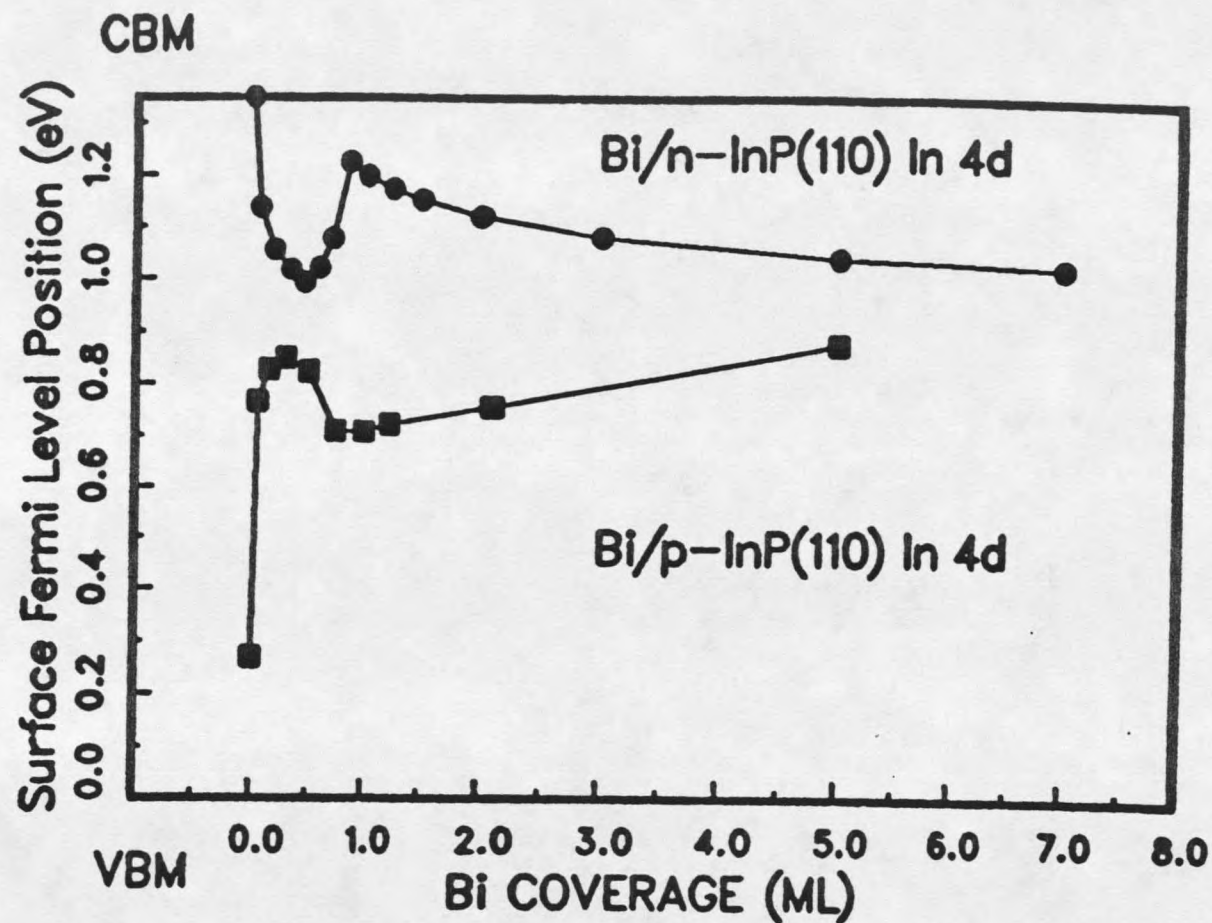


Fig. 29 Position of surface Fermi level vs. Bi coverage on both n- and p-InP(110) (both $4 \times 10^{18} \text{cm}^{-3}$). Constructed from shifts in the bulk component of the In 4d line of bulk sensitive photoemission spectra.

rapidly with coverage as in the n-type case. However, at 1 ML, unlike the n-InP case, it remains at the high value of 0.7 eV. Recent band bending results for Sb on p-InP(110) show that the band bending at 1 ML is significantly larger for Sb/p-InP(110) than for Sb/n-InP(110). Even annealing of the films does not change the essential behavior of the band bending.^{58,59,61} One interpretation which has been proposed by several groups is that for the Sb on InP(110) the chemical bonding configuration might not correspond to the bulk-extended zig-zag chain model found for Sb/GaAs(110), i.e., the Sb adatoms are proposed to form chemical bonds with only In, and not with P surface atoms.^{58,59,61} Thus, the P surface atoms with filled dangling bond states that could lie in the bulk band gap, which could donate an electron to the unoccupied acceptor-states of the p-type substrate resulting in a large band bending. However, both the recent dynamical LEED⁹⁵ and photoemission results³⁵ for Sb and Bi on InP(110) surfaces show that Sb and Bi adatoms do form chemical bonds with both In and P surface atoms, i.e., the bulk-extended zig-zag chain on (110) surface, as they do on GaAs(110). Therefore, we argue that the large band bending for Bi/p-InP (or for Sb/p-InP) is not likely due to charge transfer from the donor-like P dangling bond states, but rather is due to another process, Bi valence-band charge transfer, as we discuss below.

Fig. 29 also shows that the band bending for both n- and p-type cases changes with coverage when the Bi coverage increases beyond 1 ML. This coverage dependence will be discussed in the next section.

Electronic structure studies

To determine the evolution of the interface electronic structure for Bi/InP(110), valence band photoemission was used to monitor the occupied density of states. Figure 30 shows the angle-integrated valence band energy distribution curves (EDC) for Bi/n-InP(110) taken at room temperature with a photon energy of 29 eV for various Bi coverages. The energy reference of the spectra is the conduction band maximum (CBM) of the bulk InP. The clean surface spectrum (on the bottom) shows that the valence band maximum (VBM) is at ~ 1.35 eV below the Fermi level (E_F), indicating a flat-band unpinned n-type surface. The feature A corresponding to the Bi-induced states, appears at 0.75 eV below the VBM for coverages above 1/3 ML, we identify this Bi-induced state as a Bi overlayer state feature⁷⁷, since its main feature (the peak shape) stays constant for coverages from 0.75 ML up to 7 ML. Furthermore, this state appears to be associated with the formation of the two-dimensional Bi patch, since the feature for this state cannot be observed below 1/3 ML.

The observation that the Bi-induced states lie in the InP band gap is most interesting for determining the electronic characters of the Bi overlayers. The spectra for the valence band edge were measured very carefully, with small steps of 25 meV and good statistics. Figure 31 shows resulting EDC's for the region around the valence band edge for Bi on both n- and p-type InP(110). The energy reference for the EDC's is the bulk InP conduction band maximum (CBM) for n-type, and the valence band minimum (VBM) for p-type. The Fermi level (E_F) is also labeled on

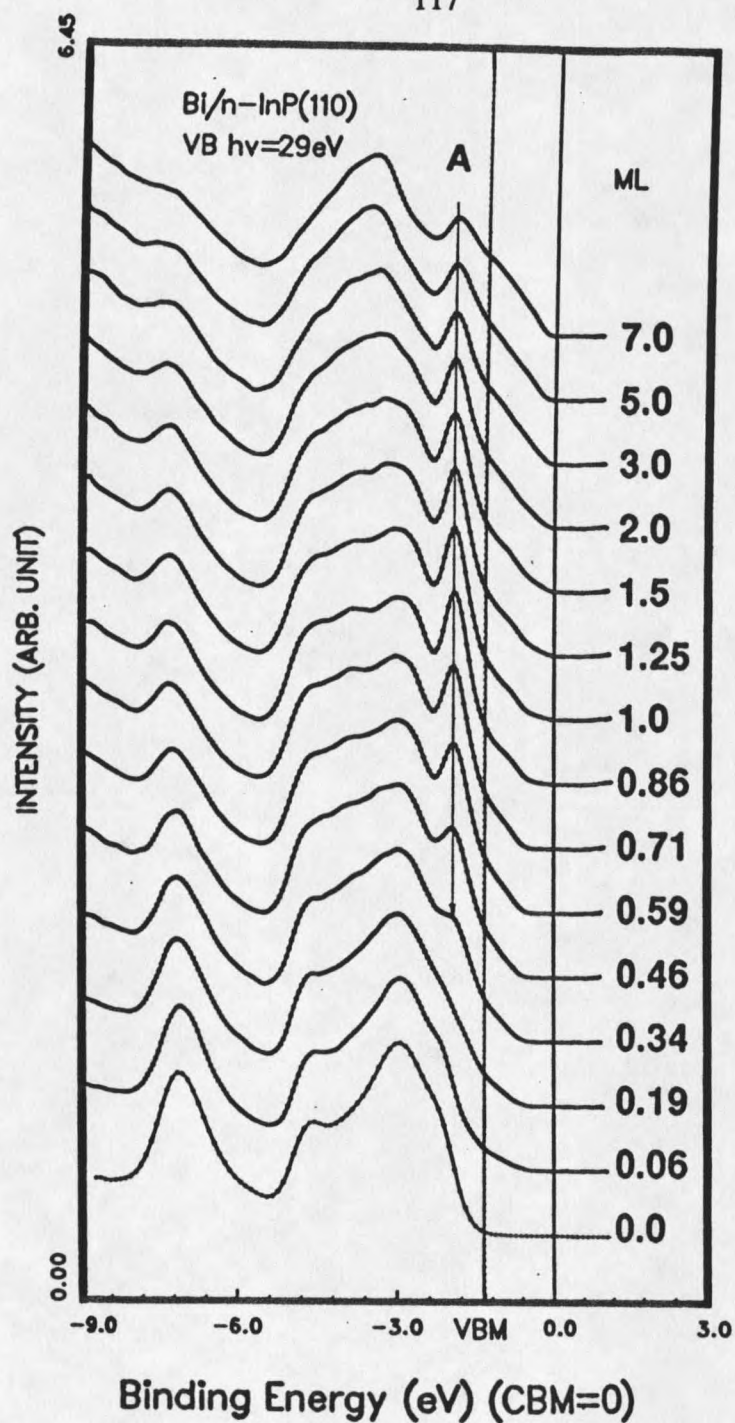
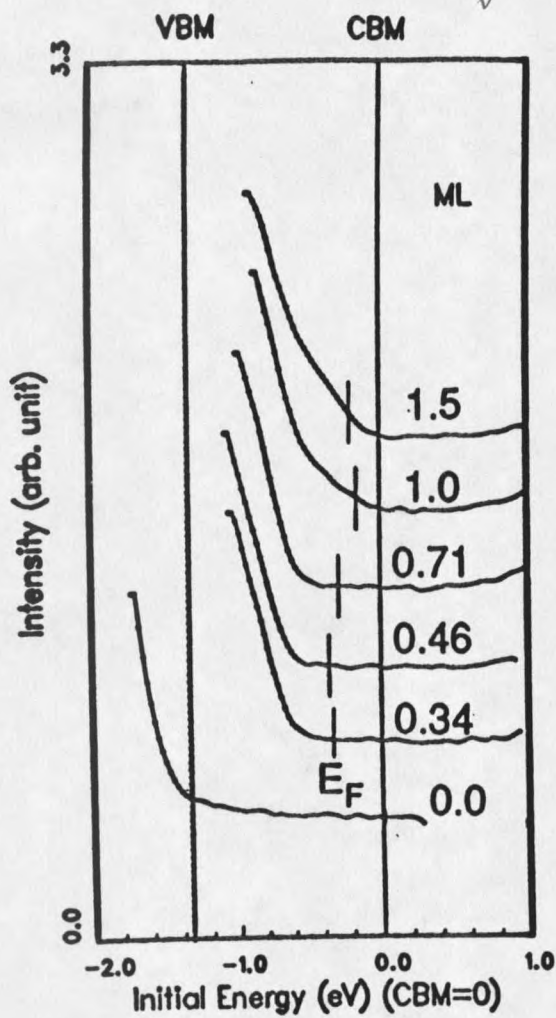
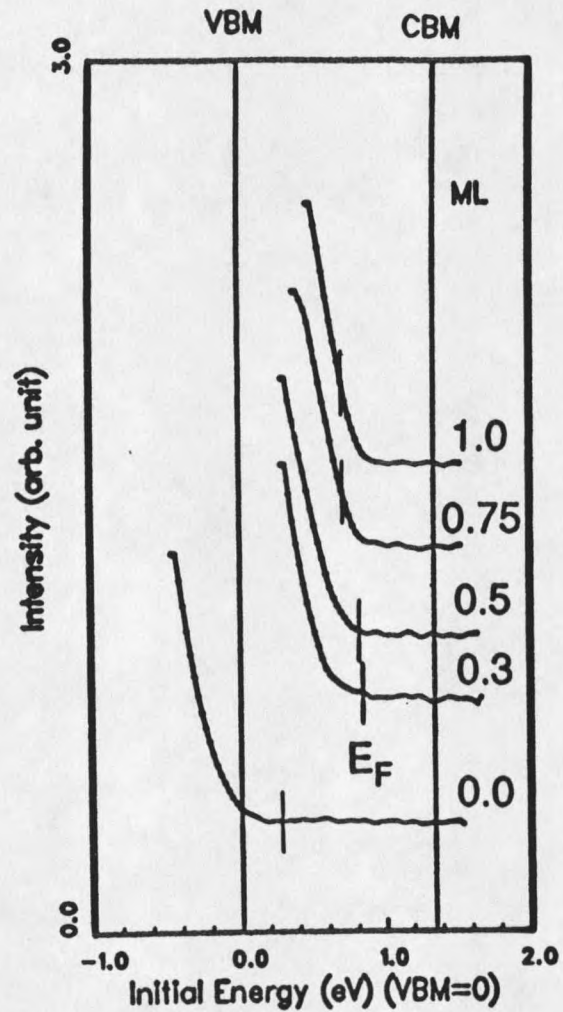


Fig. 30 Angle-integrated valence band energy distribution curves (EDC) for the Bi/n-InP(110) taken at room temperature with a photon energy of 29 eV for various Bi coverages.



Bi/n-InP(110)
VB $h\nu=29$ eV

(a)



Bi/p-InP(110)
VB $h\nu=29$ eV

(b)

Fig. 31 EDC's of the emission edge for Bi on n- and p-InP(110). The spectra are referred to the bulk InP CBM for n-type, VBM for p-type.

each spectrum. For the n-type sample, up to about one monolayer, the Bi overlayers are distinctly semiconducting, since the onset of emission due to Bi induced-states are 0.3 eV below E_F for $\sim 1/3$ ML, and approaches E_F for high coverage (see Fig. 31(a)). It takes ~ 1.5 ML's for emission to appear at E_F , indicating the formation of the (semi)metallic overlayers. However for p-InP, there is emission at the Fermi level already for coverages at as low as $3/4$ ML and perhaps lower (see Fig. 31(b)). The observed (semi)metallic behavior at well below a full monolayer, is very interesting and is quite different than the behavior of the n-type case. On the other hand, the spectra in Fig. 30, show that with increasing coverages from 0.3 ML to 1 ML, the Bi emission onset for n-type extends from the mid-gap to the CBM, but for p-type, it stays in the mid-gap.

To understand the difference in the photoemission edge for n-type vs p-type substrates, we note that the density of Bi-induced states is independent of the substrate doping. Thus, the difference in the Bi emission edge photoemission results stems only from the fact that these states are not occupied for the p-type material because of the charge transfer process, as we discuss below.

Charge Transfer Model

Low coverage case

To discuss the charge transfer established from the above data analysis in some

detail, we refer to Fig. 32, in which we sketch the energy-level diagrams of InP and densities of Bi induced states, using the EDC's of the 1 ML Bi overlayer on n- and p-type InP(110). One can see that for the 1 ML Bi/n-InP, where the Bi induced emission onset extends nearly to CBM, there is almost no band bending. This means if the system could be separated into two parts, the Bi-overlayer and InP substrate, E_F of the Bi overlayer would be almost at the same position in the gap as E_F for the substrate (i.e., CBM). Thus, one expects no charge adjustment would occur when these two parts contact each other, the Bi states in the gap would remain filled as shown in Fig. 32. While for the 1 ML Bi/p-InP, E_F of the Bi overlayer now is almost 1.3 eV higher than E_F of the flat-band substrate. To achieve a common Fermi level, the electrons in the Bi-induced states above the VBM must transfer to the substrate so that E_F of the Bi overlayer drops to the mid-gap, forming a large band bending on the substrate side of the junction. The charge-neutrality condition is given by

$$Q_{sc} = -Q_{ad} \quad (7.2)$$

where Q_{ad} is the total charge per unit area carried by the Bi adatoms, and Q_{sc} is the space charge of the substrate. The amount of the charge transfer from Bi induced states (i.e., the density of the unoccupied state) could be obtained from Eq. (7.2) with a determination of Q_{sc} . The latter can be estimated from the band bending of 0.7 eV using the step model¹³; the charge Q_{sc} turns out to be $\sim 6.2 \times 10^{12} \text{ cm}^{-2}$. On the other hand, one can crudely estimate the density of those unoccupied states by comparing

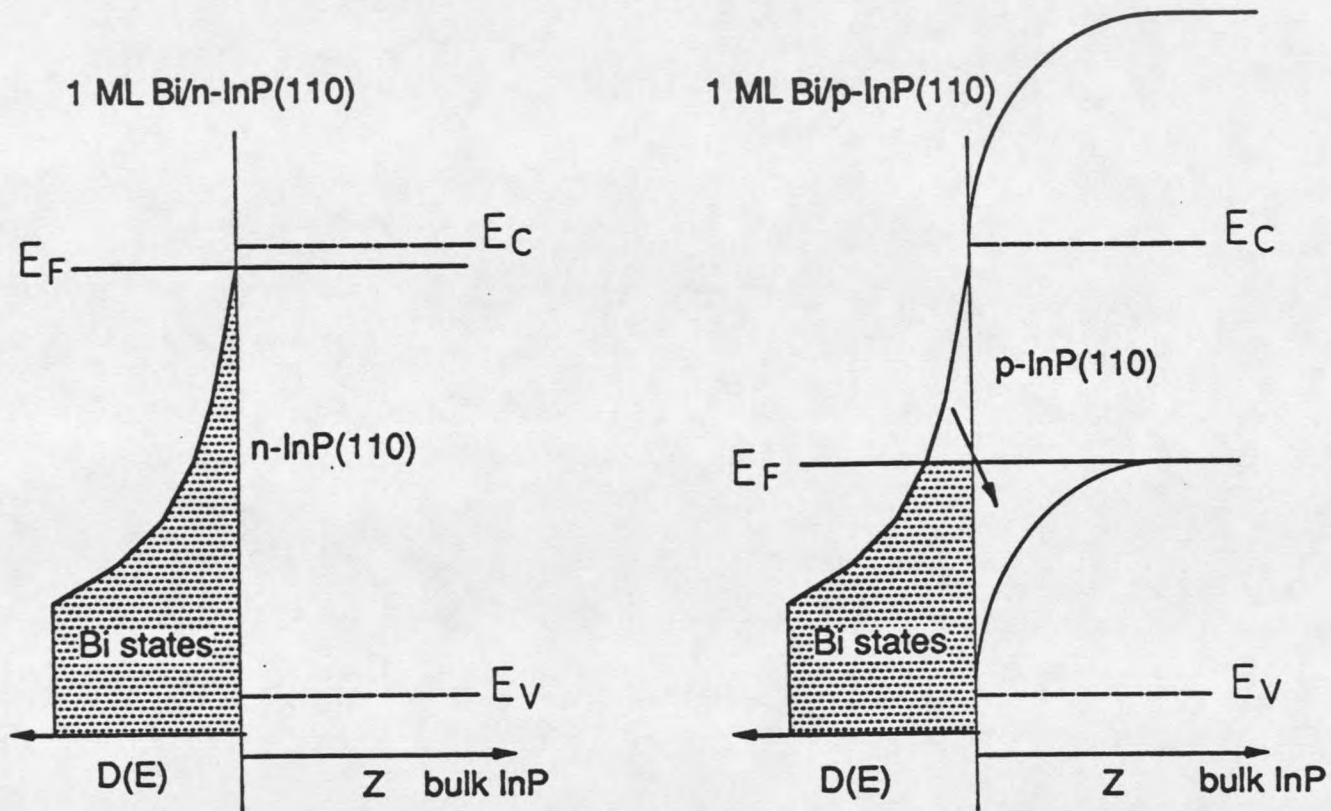


Fig. 32 Energy-level diagrams of InP and schematic densities of states of the Bi overlayer on n- and p-InP(110) at 1 ML. The charge transfer process is shown by the error.

the area of the difference between the 1 ML n-type EDC and the 1 ML p-type EDC in the gap, shown in Fig. 32, with the area of the EDC corresponding to Bi p-like occupied states ($3 \times 8.21 \times 10^{18} \text{ cm}^{-2}$). This estimate gives for the density of states $\sim 6.5 \times 10^{12} \text{ cm}^{-2}$, which is quite close to the value given by Eq. (7.2) above.

High coverage case

In the earlier discussion of the band bending, we mentioned that the band bending also has a coverage dependence for high coverages ($>1 \text{ ML}$). Here we would like to discuss this coverage dependence in terms of the charge transfer. Figure 33 shows similar spectra for the Bi/n-InP(110) as in Fig. 31(a), but for higher coverage (from 1 ML to 7 ML). One notes that the emission onset for the Bi states (i.e., E_F) moves back slightly toward the mid-gap as the equivalent number of ML's increases. The movement of E_F shown in Fig. 33 as well as Fig. 29, could be attributed to the Bi layer transition from a two-dimensional- to three-dimensional-like electronic structure. That is the Bi layer size effect discussed in Chapter VI. Let us now consider the two limiting cases: bulk Bi and submonolayer Bi. For the former, i.e., a typical semimetal, the conduction band minimum CBM_{Bi} overlaps with VBM_{Bi} at the Fermi level, while for the semiconducting Bi (the submonolayer Bi), CBM_{Bi} is higher than VBM_{Bi} with a gap E_g . When the size effect occurs as the Bi coverage increases, a gradual transition from the semiconductor to semimetal behavior occurs. Therefore, CBM_{Bi} moves downward to reach VBM_{Bi} and the gap vanishes. In Fig. 31, the

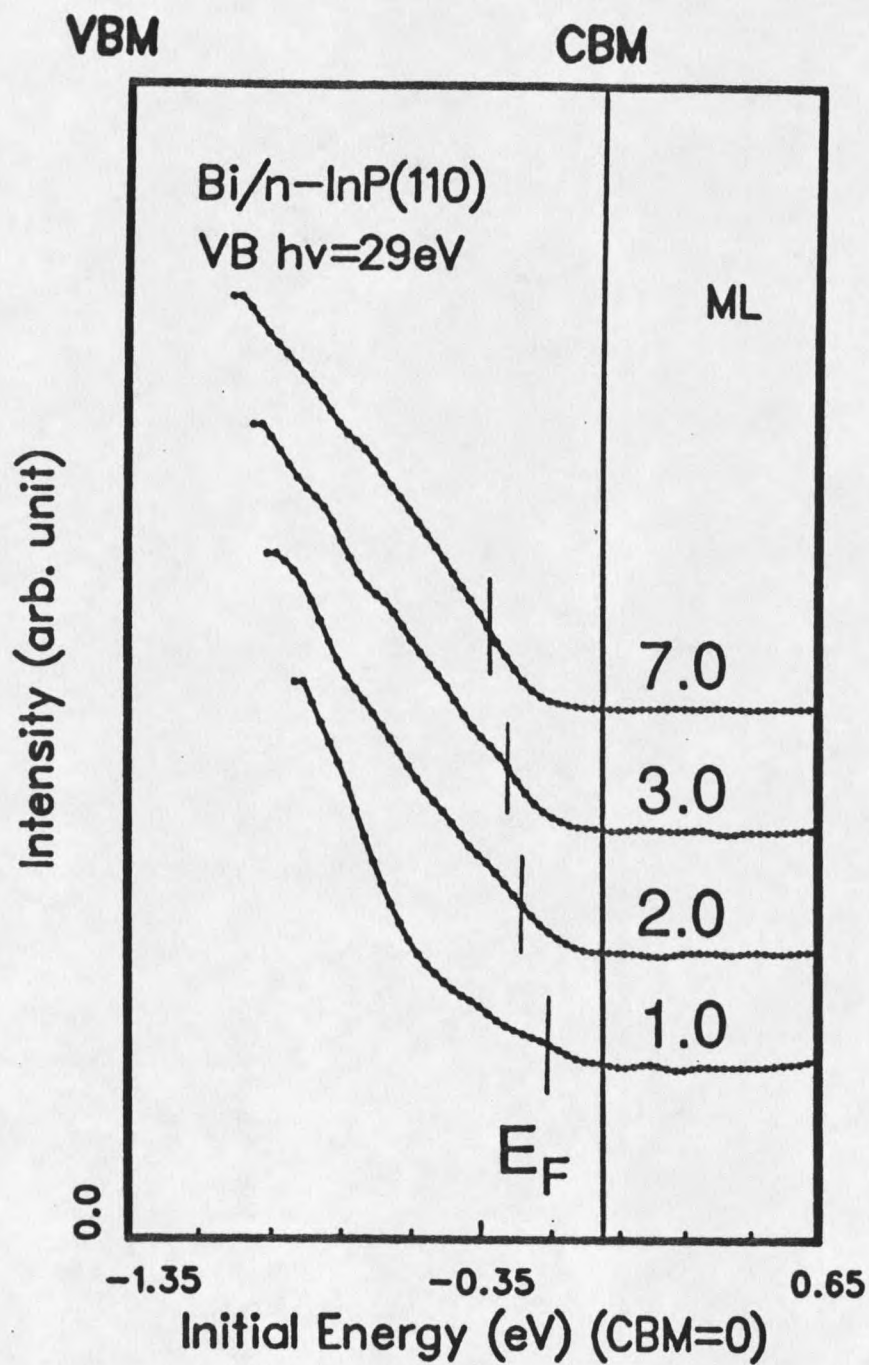


Fig. 33 High coverage EDC's of the emission edge for Bi/n-InP. The spectra are referred to the bulk InP CBM.

evidence is presented showing that VBM_{Bi} moves up to reach E_F as the coverage increases. Evidences for CBM_{Bi} moving downward to reach E_F can be found in inverse photoemission data for Bi/InP(110).⁸¹ At the 1 ML coverage, CBM_{Bi} could be considered to just meet the VBM_{Bi} , since the onsets for the photoemission EDCs and inverse photoemission PDCs (photon energy distribution curves⁸¹) are at E_F . For coverages above 1 ML overlap of CBM_{Bi} and VBM_{Bi} occurs, and the electrons from the filled states at VBM_{Bi} start to transfer to the unoccupied states at CBM_{Bi} . As a result, E_F shifts to the lower energy.

Schottky Barrier Model for Bi/InP(110)

Finally we will briefly discuss the barrier model for the Bi/InP(110). As we discussed above, in the submonolayer regime, the barrier formation could be attributed to the interface states at the peripheries of Bi terraces observed in STM investigation. At 1 ML, most of the interface states have evidently been eliminated so that the barrier height for the n-type case decreases to near-zero. The large barrier height for the p-type is due to the process of charge transfer involving the Bi valence band, and not the appearance of additional interface states. The change of the barrier height above 1 ML, can be explained as a result of the change of the Bi electronic structure. Therefore, in the regime above 1 ML, the band bending for Bi/InP(110) interfaces can be well described by the Schottky model.

On the other hand, we can verify this model by comparing the measured value of the high coverage band bending with the value given by the Schottky limit (Eq. (7.1)). For Bi/InP interfaces, we obtain from the literature that the InP electron affinity χ_{SC} is ~ 4.4 eV and the Bi work function Φ_M is 4.4 eV,⁵⁸ so the Schottky value for the band bending is around zero eV. In fact, the band bending could be a bit higher than zero, because the InP electron affinity χ_{SC} could be changed after Bi deposition. Evidence of such a behavior has been observed in the Sb/GaAs(110) case where the GaAs electron affinity is reduced by 0.2 eV,^{65,71} which is attributed to the Sb layer healing out the surface relaxation for the cleaved surface. For instance, if χ_{SC} for InP is reduced to 4.1-4.2 eV, the model band bending would be 0.2-0.3 eV, which is quit close to the measure value (~ 0.35 eV) for Bi/n-InP at 7 ML (see Fig. 29). Thus the thick Bi/InP(110) barriers appear to be the Schottky limit.

CHAPTER VIII

CONCLUSIONS

In this thesis, we have studied the collective excitations and the Schottky barrier formation at III-V semiconductor surfaces and interfaces, using HREELS and synchrotron radiation photoemission spectroscopy.

First, we studied the hole plasmon excitations in the valence-band of heavily doped p-GaAs(110) surfaces, using HREELS. For the first time, a single well defined surface hole plasmon peak was observed, with the use of extremely heavy doping ($2.2 \times 10^{19} \text{cm}^{-3}$) and low temperature (80 K). We demonstrated that this peak is due to a coherent excitation of both light-holes and heavy-hole plasmas, and its energy position is higher than that expected by either the surface light-hole or heavy-hole plasmon. We have quantitatively analyzed our observations using local dielectric theory and shown that the large peak width of the surface hole plasmon (60 meV) is due to the low electronic mobility of holes rather than the hole plasmon dispersion.

A reversible temperature dependence of the surface hole plasmon peak was also observed. That is, the energy position and width of the surface hole plasmon peak change with temperature. We demonstrated that this temperature effect is due to the

temperature dependence of the surface scattering process, in conjunction with the kinematical factor, and not the thermal activation.

We also showed that when the peak width for the surface hole plasma is comparable to the plasmon energy in p-GaAs, the observed peak position is no longer determined only by the plasmon energy, but also by the kinematical factor. Thus, especially in the HREELS model calculation, the kinematic factor must be taken into account.

In addition, we found that, unlike for the n-GaAs system, the study of the hole plasmon-phonon coupling is more difficult than the electron plasmon-phonon since the large scattering rate can damp out all the coupling features.

In the second part of the thesis, we studied collective excitations in the overlayer system, such as, Bi/GaAs(110), ZnSe/GaAs(110), and ZnSe/Bi/GaAs(110).

For Bi/GaAs(110), we found a significant monotonic background develops with coverages, and reaches its maximum at a film thickness of 4 ML, and decreases again. We show this is due to the development of the Bi two-dimensional electron plasmon mode with coverages. We have quantitatively analyzed the experimental data using a three-layer model. The data analysis shows that the Bi overlayer undergoes a transition from a semiconductor to a semimetal starting at 1.5 ML.

For ZnSe/GaAs(110), we found a phonon peak initially at 35 meV changes with ZnSe coverages in terms of the peak position and the lineshape. We show this change occurs because the observed peak is a convolution of the surface ZnSe mode

and the interface GaAs mode, both the energy position and the shapes of the phonon peak depend on the intensities of the two individual modes. A good agreement between theory and experiment has been obtained.

We also studied the ZnSe/Bi/GaAs(110) sandwich system with various coverages of ZnSe. It was found that a rapid shift for the phonon peak occurs at a ZnSe coverage of only 1-2 ML. This is consistent with the calculation results of a four-layer model. The data analysis shows the collective excitation (long wavelength optical phonon) for ZnSe exists in the one monolayer, and even in submonolayer regime.

In the last part of this thesis, we turned to a new subject, the study of the Schottky barrier formation at both Bi/n- and p-InP(110) interfaces, using synchrotron radiation photoemission spectroscopy.

The high-resolution core-level results indicate the Bi/InP(110) interface is a model system, i.e., an ordered and nondisruptive interface. The results further reveal a Stranski-Krastanov growth mode. That is, in the 0-1 ML regime, Bi atoms are bonded to surface In and P atoms, Above 1 ML, clustering of additional Bi adatoms occurs.

A unique band bending is observed in the region of a few monolayers for both n- and p-type cases. At the submonolayer regime, we interpret the band bending as a result of the presence of the interface states which are created by the irregularities of the Bi layer and peripheries of Bi terraces. For coverages above 1 ML, the band

bending is controlled by a charge transfer process. We propose this charge transfer model on the basis of the observed difference in the photoemission spectra of the Bi emission edges for the n- and p-type samples.

Our studies suggest that the Bi/InP(110) interface be an interface that is free of interface states.

REFERENCES

REFERENCES

1. R. Matz and H. Luth, Phys. Rev. Lett. **46**, 500(1981).
2. A. Ritz and H. Luth, Phys. Rev. Lett. **52**, 1242(1984).
3. A. A. Lucas and M. Sunjic, Phys. Rev. Lett. **26**, 229 (1971).
4. H. Ibach and D. L. Mills, Electron Energy Loss Spectroscopy and Surface Vibrations(Academic, New York, 1982).
5. E. Evans and D. L. Mills, Phys. Rev. B **5**, 4126(1972).
6. Ph. Lambin, J. P. Vigneron, and A. A. Lucas, Phys. Rev. B **32**, 8203(1985).
7. R. G. Egdel, W. R. Flavell, Z. J. T. Gray-Grychowski, R. A. Stradling, B. A. Joyce, and J. H. Neave, J. Electron Spectrosc. Related Phenomena **45**, 177(1987).
8. Yuan Meng, J. Anderson, J. C. Hermanson, and G. J. Lapeyre, Phys. Rev. B. Rapid Comm. (in press)
9. Z. J. T. Gray-Grychowski, R. G. Egdel, B. A. Joyce, R. A. Stradling, and K. Woodbridge, Surf. Sci. **186**, 482(1987).
10. Y. Chen, S. Nannarone, J. Schaefer, J. C. Hermanson, and G. J. Lapeyre, Phys. Rev. B **39**, 7653(1989).
11. Y. Chen, J. C. Hermanson, and G. J. Lapeyre, Phys. Rev. B **39**, 12682(1989).
12. I. Egri, R. Matz, H. Lüth and A. Stahl, Surf.Sci., **128**, 51(1983).
13. Y. Chen, Yabo-Xu and G.J. Lapeyre, J. Vac. Sci. Technol., **A6(3)**, 686(1988).
14. Joseph A. Stroscio and W. Ho, Phys. Rev. Lett., **54**, 1573(1985).
15. Y. Goldstein, A. Many, I. Wagner and J. Gersten, Surf.Sci., **98**, 599(1980).
16. A. Many, I. Wagner, A. Rosenthal, J. I. Gersten and Y. Goldstein, Phys. Rev. Lett., **46**, 1648(1981).
17. A. Many, J. I. Gersten, I. Wagner, A. Rosenthal and Y. Goldstein, Surf. Sci., **113**, 355(1982).

18. J. I. Gersten, I. Wagner, A. Rosenthal, Y. Goldstein, A. Many and R. E. Kirby, Phys. Rev. **B 29**, 2458(1984).
19. S. R. Streight and D. L. Mills, Phys. Rev. **B 37**, 965(1988).
20. D. H. Ehlers and D. L. Mills, Phys. Rev. **B 34**, 3939(1986).
21. D. H. Ehlers and D. L. Mills, Phys. Rev. **B 36**, 1051(1987).
22. L. H. Dubois, B. R. Zegarski and B. N. J. Persson, Phys. Rev. **B 37**, 9128(1987).
23. J.E Demuth, B. N. J. Persson, and A. J. Schell-Sorokin, Phys. Rev. Lett., **51**, 2214(1983).
24. Bingruo Xu and J. C. Hermanson, Phys. Rev. **B 40**, 12539(1989).
25. B. N. J. Persson and J. E. Demuth, Phys. Rev. **B 30**, 5968(1984).
26. Yuan Meng, J. Anderson, and G. J. Lapeyre, Submitted to Phys. Rev. B.
27. J.E. Demuth and B.N.J. Persson, Phys. Rev. Lett. **54**, 584(1985).
28. A. Ritz and H. Luth, Phys. Rev. **B 32**, 6596(1985).
29. J.M. Layet, R. Contini, J. Derrien and H. Luth, Surf. Sci., **168**, 142(1986).
30. L.H. Dubois, G.P. Schwartz, R.E. Camley, and D.L. Mills, Phys. Rev. **B 29**, 3208(1984).
31. Yuan Meng, J. Anderson, and G. J. Lapeyre, (to be submitted).
32. Annovi, Maria Grazia Betti, U. del Pennino, and Carlo Mariani, Phys. Rev. **B 41**, 11978(1990).
33. J. J. Joyce, J. Anderson, M. M. Nelson, and G. J. Lapeyre, Phys. Rev. **B 40**, 10412 (1989).
34. J. J. Joyce, J. Anderson, M. M. Nelson, C. Yu, and G. J. Lapeyre, J. Vac. Sci. Technol. **A 40**, 850 (1989).
35. J. J. Joyce, M. M. Nelson, Ming Tang, Y. Meng, J. Anderson, and G. J. Lapeyre,

- J. Vac. Sci. Technol. A **8**, 3542 (1990).
36. G. D. Waddill, C. M. Aldao, C. Capasso, P. J. Benning, Yongjun Hu, T. J. Wagener, M. B. Jost, and J. H. Weaver, Phys. Rev. B **41**, 5960 (1990).
37. Yongjun Hu, T.J. Wagener, M.B. Jost, and J.H. Weaver, Phys. Rev. B **40**, 1146(1989).
38. T. Guo, R.E. Atkinson, and W.K. Ford, Phys. Rev. B **41**, 5138(1990).
39. A. B. Mclean, R. M. Feenstra, A. Taleb-Ibrahimi, and R. Ludeke, Phys. Rev. B **39**, 12925 (1989).
40. W. K. Ford, T. Guo, S. L. Lantz, K. Wan, S. L. Chang, C. B. Duke, and D. L. Lessor, J. Vac. Sci. Technol. B **8**, 940 (1990).
41. J. Petruzzello, B. L. Greenberg, D. A. Cammack, and R. Dallby, Appl. Phys. Lett., **63**, 2299(1988).
42. D. J. Olego, Appl. Phys. Lett., **51**, 1422(1987).
43. Yuan Meng, M. M. Nelson, J. Anderson, and G. J. Lapeyre, J. Vac. Sci. Technol. A **8**, 2667(1990).
44. W. Schottky, Phys. Z. **113**, 367 (1939).
45. J. Bardeen, Phys. Rev. **71**, 717 (1947).
46. L. J. Brillson, Surf. Sci. Rep. **2**, 123 (1982).
47. V. Heine, Phys. Rev. A **138**, 1689 (1965).
48. J. Tersoff, Phys. Rev. Lett **52**, 465 (1984).
49. W. E. Spicer, P. W. Chye, P. R. Skeath, C. Y. Su., and I. Lindau, J. Vac. Sci. Technol. **16**, 1422 (1979).
50. R. H. Williams, R. R. Varma, and V. Montgomery, J. Vac. Sci. Technol. **16**, 1418 (1979).
51. W. Mönch, Phys. Rev. B **37**, 7129 (1988).

52. L. J. Brillson, Comments Cond. Mat. Phys. **14** 311 (1989) and reference therein.
53. Yuan Meng, J. J. Joyce, Ming Tang, J. Anderson, and G. J. Lapeyre, Submitted to Appl. Phys. Lett.
54. K. Li and A. Kahn, J. Vac. Sci. Technol., **A4(3)**, 958(1986).
55. C. M. Aldao, I. M. Vitomirov, F. Xu, and J. H. Weaver, Phys. Rev. **B 40**, 3711(1989).
56. T. Kendelewicz, P. H. Mahowald, C. E. McCants, K. A. Bartness, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. **B 5**, 1033 (1987).
57. A. B. Mclean and F. J. Himpsel, Phys. Rev. **B 40**, 8425(1989).
58. R. H. Williams, D. R. T. Zahn, N. Esser, and W. Richter, J. Vac. Sci. Technol. **B 7**, 997 (1989).
59. T. Kendelewicz, R. Cao, K. Miyano, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. **A 7**, 765 (1989).
60. T. Kendelewicz, K. Miyano, R. Cao, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. **B 7**, 991 (1989).
61. N. Esser, M. Reckzugel, R. Srama, U. Resch, D. R. T. Zahn, W. Richter, C. Stephens, and Hunermann, J. Vac. Sci. Technol. **B 8**, 680 (1990).
62. C. Stephens, D. R. T. Zahn, K. Fives, R. Cimino, W. Braun, I. T. McGovern, J. Vac. Sci. Technol. **B 8**, 674 (1990).
63. D. R. T. Zahn, N. Esser, W. Richter, C. Stephens, and R. H. Williams, J. Phys., Condens. Matter **1**, SB45(1989).
64. R. M. Feenstra and P. Martensson, Phys. Rev. Lett. **61**, 447(1988).
65. Monika Mattern-Klosson, R. Strumpler, and H. Luth, Phys. Rev. **B 33**, 2559(1986).
66. P. Martensson and R. M. Feenstra, Phys. Rev. **B 39**, 7744 (1989).
67. K. E. Miyano, T. Kendelewicz, R. Cao, C. J. Spindt, I. Lindau, and W. E. Spicer,

and J. C. Woicik, Phys. Rev. B **42**, 3017 (1990).

68. F. Schaffer, R. Ludeke, A. Taleb-Ibrahimi, G. Hughes, and D. Rieger, Phys. Rev. B **36**, 1328 (1987).

69. R. Ludeke, A. Taleb-Ibrahimi, R. M. Feenstra, and A. B. Mclean, J. Vac. Sci. Technol. B **7**, 936 (1989).

70. P. Skeath, C. Y. Su, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. **17**, 874 (1980); **19**, 556 (1980).

71. Monika Mattern-Klosson and H. Luth, Solid State Commun. **56** 1001 (1985).

72. P. Skeath, C. Y. Su, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. **19**, 556 (1980).

73. E. H. Rhoderick and R. H. Williams, Metal-Semiconductor Contacts, 2nd ed. (Oxford Science Publications, Clarendon, Oxford, 1988) and reference therein.

74. C. B. Duke, A. Paton, W. K. Ford, A. Kahn, and J. Carelli, Phys. Rev. B **26**, 803 (1982).

75. C. M. Bertoni, C. Calandra, F. Manghi, and E. Molinari, Phys. Rev. B **27**, 1251 (1983).

76. C. Mailhot, C. B. Duke, and D. J. Chadi, Phys. Rev. Lett. **53**, 2114 (1984).

77. C. Mailhot, C. B. Duke, and D. J. Chadi, Phys. Rev. B **31**, 2213 (1985).

78. Seeger, Semiconductor Physics (Spring-Verlag, 1989), B.K. Ridley, Quantum Processes in Semiconductors (Oxford Science Publications, 1988).

79. S. M. Sze, Physics of Semiconductor Devices (Wiley-Interscience, New York, 1981).

80. C. Kittel, Introduction to Solid State Physics (Wiley-Interscience, New York, 1986).

81. M.B. Jost, Yongjun Hu, D. M. Poirer, and J.H. Weaver, J. Vac. Sci. Technol. A (in press).

82. C. G. Olson, Nucl. Instrum. Methods Phys. Res. A2 **66**, 205(1988).
83. C. J. Powell and M. P. Seah, J. Vac. Sci. Technol. A **8**, 735(1990).
84. J. J. Joyce, M. Del Giudice, and J. H. Weaver, J. Electron Spectrosc. Relat. Phenon. **45**, 31(1989).
85. T. C. Chiang, CRC Critical Reviews in Solid State and Material Sciences, **8**, 269(1988).
86. "Electron Spectroscopy for Surface Analysis", H. Ibach, Ed., (Springer-Verlin, Berlin, 1977).
87. Ph. Lambin, J. P. Vigneron, A. A. Lucas, P. A. Thiry, M. Liehr, J. J. Pireaux, R. Caudano, and T. Kuech, Phys. Rev. Lett., **56**, 1842(1986).
88. M. Liehr, P. A. Thiry, J. J. Pireaux and R. Caudano, Phys. Rev **B 34**, 7471(1986).
89. H. Bilz, W. Kress, Phonon Dispersion Relations in Insulators (Spring Series in Solid-State Sciences, New York, 1979).
90. M. M. Nelson, J. J. Joyce, Y. Meng, J. Anderson, and G. J. Lapeyre, (in preparation).
91. A. Zangwill, Physics at Surface (Cambridge University Press, New York, 1988).
92. W. L. Schaich, Phys. Rev **B 34**, 686(1981).
93. J. D. Jackson, Classical Electrodynamics (John Wiley & Sons, New York, 1975).
94. 70. S. J. Eglash, M. D. Williams, P. H. Mahowald, N. Newman, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. **B 2**, 481(1984).
95. N. W. Ashcroft and N. D. Mermin, Solid State Physics (Saunders College, Philadelphia, 1976).
96. T. Guo, K. J. Wan, W. K. Ford, and C. B. Duke (to be published).

MONTANA STATE UNIVERSITY LIBRARIES



3 1762 10051311 6

HOUCHEN
BINDERY LTD
UTICA/OMAHA
NE.